Synthetic, Structural and Spectroscopic Studies on Osmium(III) Carboxylates and Arene Ruthenium(II) Complexes

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Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results presented have already been published.

To Joanne

Acknowledgments

I wish to thank Dr. T.A. Stephenson for his constant help, encouragement and enthusiasm throughout this work. I also wish to express my gratitude to Drs. R.O. Gould and L. Sawyer for determining the crystal structures of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$ and $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)\text{-}Cl(C_4H_4N_2)_2][PF_6]$ respectively and to Drs. R.O. Gould and M.D. Walkinshaw for their assistance with the other crystallographic determinations reported here. I also wish to thank Drs. D.R. Robertson, T. Arthur and I.W. Robertson for their pioneering studies in the field of areneruthenium(II) chemistry and Dr. M.A. Bennett for some of the results reported in Chapter 1. In addition, I am grateful to Mr. L.H. Bell and Mr. J.R.A. Millar for recording many of the N.M.R. spectra, Mr. M. Grumbaum for performing microanalytical measurements and to Dr. G. Hunter (University of Dundee) for the use of his Faraday balance. I am deeply indebted to the S.E.R.C. for their financial support and the University of Edinburgh for use of facilities. Finally, my thanks to Miss A. Erskine for typing this thesis.

ABSTRACT

Chapter 1 describes the synthesis of complexes $Ru(\eta\text{-arene})X(O_2CR)$ by three synthetic routes, viz. by reaction of $[Ru(\eta\text{-arene})X_2]_2$ with: (a) $RCO_2H/(RCO)_2O$, (b) $Na[O_2CR]$/acetone, and (c) $Ag[O_2CR]$ (1:2 mol ratio). In addition the synthesis of the complexes $Ru(\eta\text{-arene})(O_2CR)_2$ by reaction with $Ag[O_2CR]$ (1:4 mol ratio) is described. The reactions of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ with potentially binucleating ligands, to give cations $[Ru(\eta\text{-}C_6H_6)ClL_2]^+$, and with NaOR/ROH (R = Me, Et) to give $[Ru_2(\eta\text{-}C_6H_6)_2(OR)_3]^+$, are discussed. The synthesis of analogous mononuclear complexes by reaction of $[M(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (M = Ru, Os) with binucleating ligands is presented and the crystal structure of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_4N_2)_2][PF_6]$ reported.

Chapter 2 discusses the formation and crystal structure determinations of the unusual hydroxo bridged tetranuclear complexes $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$. The synthesis and characterisation of complexes containing triply bridging -OH, -OR (R = Me, Et, ^{i}Pr, ^{i}Bu, Ph) and -SEt ligands is described. The reactions of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, $1,4\text{-}MeC_6H_4CHMe_2$) with $Na[O_2CR]$ (R = Me, CF_3) are discussed and the crystal structure of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4\text{-}CHMe_2)_2Cl_3][BPh_4].MeOH$ reported. The synthesis of the complexes $[Ru(\eta\text{-arene})X_2]_2$ and the cations $[Ru_2(\eta\text{-arene})_2X_3]^+$

by reaction of several of the hydroxo and methoxo species, described earlier, with HX (X = Cl, Br, I) is reported, together with preliminary studies on a variety of other reactions.

Chapter 3 describes a new high yield route to a variety of mixed-sandwich cations $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ (M = Ru, Os) by reaction of the appropriate dimer $[M(\eta\text{-arene})Cl_2]_2$ with a four fold excess of $Tl[C_5H_5]$ in CH_3CN. The n.m.r. and electrochemical properties are reported together with the results of an investigation of the reactivity of these complexes and comparison made with the appropriate properties of the well known $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations.

Chapter 4 discusses the synthesis of the new complexes $Os_2(O_2CR)_4Cl_2$ (R = Me, C_2H_5, $^nC_3H_7$, CH_2Cl) and their characterisation by a variety of techniques. The crystal structure determination of $Os_2(O_2C^nC_3H_7)_4Cl_2$ is reported. The formation of the bridged diosmium complexes $Os_2(hp)_4Cl_2$ and $Os_2(ONHCCF_3)_4Cl_2$ by reaction of $Os_2(O_2CMe)_4Cl_2$, with Hhp and CF_3CONH_2 respectively, is reported together with the results of an investigation into the reactions of this compound with Lewis bases (bipy, phen, diphos) and acids (HX, Hacac). An examination of the electronic spectra and magnetic properties of these binuclear carboxylates indicates that there is considerable antiferromagnetic interaction between the paramagnetic osmium ions.

Appendix I presents the results of the crystal structure determination of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$.

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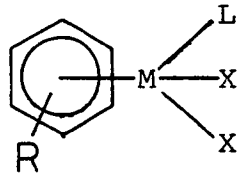
CHAPTER 1

Synthesis and Reactions of

η^6-Arene Ruthenium(II) Carboxylates

1.1 Introduction

The work presented in Chapters 1-3 of this thesis is concerned with the chemistry of species containing arenes π-bonded to ruthenium(II) and osmium(II) centres. These complexes fall into three distinct categories namely: (i) monomeric, neutral or monocationic species, $[M(\eta^6\text{-arene})LX_2]$ (1) and $[M(\eta^6\text{-arene})L_2X]^+$ (M = Ru, Os; arene = C_6H_6 and substituted benzenes; L = C_5H_5N, PR_3 etc.; X = Cl, Br, I); (ii) mixed sandwich cations, $[M(\eta^6\text{-arene})(\eta^5\text{-}C_5H_5)]^+$ (2) (M = Ru, Os), and (iii) binuclear triple bridged cations, which can be considered as extended sandwich compounds, $[M_2(\eta^6\text{-arene})_2X_3]^+$ * (3) (M = Ru, Os; arene = C_6H_6, substituted arenes; X = halogens, OH, OMe, OEt).



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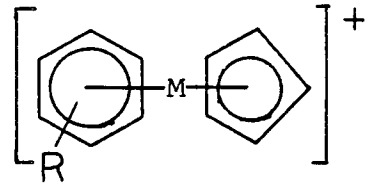

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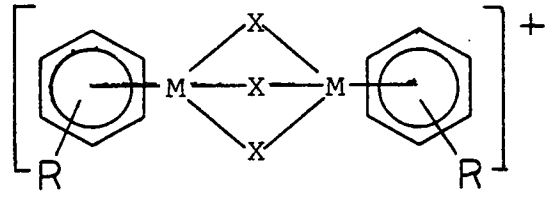
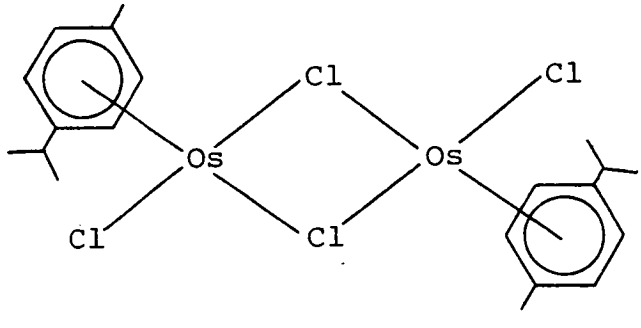


(3)

* All further references to η^6-arenes will omit the 6.

The η-arene can be considered formally as a terdentate ligand occupying three adjacent sites about an octahedrally coordinated metal centre. These ligands are good π-acceptors and hence stabilise metals in low oxidation states. Thus both M(O)(d^8) and M(II)(d^6) (M = Ru, Os) compounds are well known, although only the latter is of interest in this work.

The reaction of purified "$RuCl_3xH_2O$" with a variety of substituted cyclohexadienes in ethanol give dark-red dimeric complexes of general formula $[Ru(\eta\text{-arene})Cl_2]_2$ [1-5]. These complexes, although initially believed to be polymeric, are now accepted as being dinuclear in nature and isostructural with the well known $[M(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (M = Rh, Ir) complexes. Similarly reaction of Na_2OsCl_6 with 1,3-cyclohexadiene or α-phellandrene (5-isopropyl-2-methylcyclohexa-1,4-diene) gives $[Os(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) respectively and the dimeric nature of the osmium species has been confirmed by the X-ray structural determination of (4) [6].



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These complexes provide a convenient starting point for the syntheses of a wide range of η-arene ruthenium(II) and osmium(II) species. Before proceeding further it is worthwhile to consider typical reactions undergone by these dimeric complexes. Only reactions giving rise to monomeric complexes are discussed here; those giving dinuclear or polynuclear products will be presented in Chapter 2.

There are two general categories of reaction to consider. In non-polar solvents, reaction with an excess of a Lewis base (L) results in bridge cleavage and insertion of the ligand, L, into the vacant coordination site, with no loss of chloride ion. In contrast, if the reaction is carried out in a polar solvent then displacement of one chloride ion is accompanied by the coordination of two molecules of L and the resultant formation of a monocationic product (Equations [1] and [2]).

$$[M(\eta\text{-arene})Cl_2]_2 + L \xrightarrow[\text{solvent}]{\text{non-polar}} 2\ M(\eta\text{-arene})Cl_2L \quad \ldots\ldots\ [1]$$

$$[M(\eta\text{-arene})Cl_2]_2 + L \xrightarrow[\text{solvent}]{\text{polar}} 2[M(\eta\text{-arene})ClL_2]^+ \quad \ldots\ldots\ [2]$$

When the ligand is an anionic bidentate ligand, some modification of this scheme becomes necessary. For example, reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with thallium(I) acetylacetonate gives the neutral complex $Ru(\eta\text{-}C_6H_6)Cl(acac)$ [7]. A substantial number of all three types of product have been reported to date. Thus, reaction with amines gives the

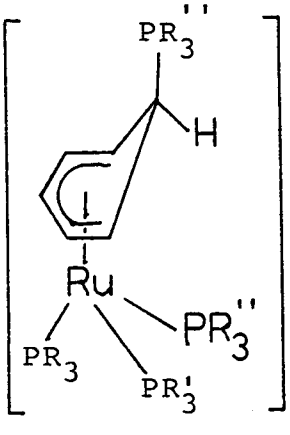
mononuclear 1:1 adducts[5,8,9] and ionic 1:2 and 1:3 adducts are also well known, e.g. $[Ru(\eta\text{-arene})L_2Cl]^+$ (L = NH_3 [10,11], py [9]; L_2 = o-phen, 2,2'-bipy[12,13] and en) and $[Ru(\eta\text{-arene})L_3]^{2+}$ (L = NH_3 [15], NH_2NR_2 and py [14]). Under forcing conditions, or longer reaction times, the arene ring may be displaced. Thus reaction of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]X$, with pyridine gives initially the $[Ru(\eta\text{-}C_6H_6)Clpy_2]^+$ cation which then reacts further to yield trans-$RuCl_2py_4$ [10,16]. Similarly prolonged interaction between $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ and 1,10-phenanthroline in methanol results in the formation of the dicationic $[Ru(phen)_3]^{2+}$ [13] ion.

Reactions with tertiary phosphines and phosphites form analogous complexes to those described for the nitrogen containing donors. The mono adducts have been known for some time[1-5,10], while the bis[17] and tris[18,19] adducts have only been reported more recently. Werner has reported[55] the synthesis of an extensive range of compounds of the type $Ru(\eta\text{-arene})X_2L$ (L = CO, $P(OMe)_3$, various PR_3) which react further with $Ag[PF_6]$ in acetone to give the monocationic compounds $[Ru(\eta\text{-arene})X(L)(acetone)][PF_6]$ and the binuclear complexes $[Ru_2(\eta\text{-}C_6H_6)_2(\mu\text{-}X)_2L_2][PF_6]_2$. The analogous compounds $[Ru(\eta\text{-arene})X(PR_3)_2][PF_6]$ were prepared by reaction of $Ru(\eta\text{-arene})X_2L$ with PR_3 and $NH_4[PF_6]$ in methanol. The ruthenium(O) complexes $Ru(\eta\text{-arene})(PR_3)_2$ and $Ru(\eta\text{-arene})(PMe_3)L$ have been prepared by the reduction of $[Ru(\eta\text{-arene})X(PR_3)_2][PF_6]$ and $[Ru(\eta\text{-arene})X(PMe_3)L][PF_6]$ respectively with sodium

naphthalide[56]. These react further with $NH_4[PF_6]/CF_3CO_2H$ to form ruthenium(II) hydrides, $[Ru(\eta\text{-arene})H(PR_3)_2][PF_6]$ and $[Ru(\eta\text{-arene})H(PMe_3)L][PF_6]$, while reaction with CH_3I results in the formation of the cations $[Ru(\eta\text{-arene})CH_3(PR_3)_2]^+$ and $[Ru(\eta\text{-arene})CH_3(PMe_3)L]^+$. Displacement of the arene will also occur under the influence of an excess of phosphine. Thus the well known cation $[Ru_2(PMe_2Ph)_6Cl_3]^+$ is formed when $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ is refluxed with PMe_2Ph for 8-12 hours[5].

Generally reaction of ruthenium(II) arene complexes with nucleophiles leads to extensive decomposition. However in the case of the tris adducts, stable η^5-cyclohexadienyl complexes have been observed. For example hydride ion will attack the benzene ring of $[Ru(\eta\text{-}C_6H_6)\{HB\text{-}(pyrazoly)_3\}]^+$ [20,21] to give a product containing a η^5-cyclohexadienyl ring. The benzene ring in the complexes $[Ru(\eta\text{-}C_6H_6)ClL_2][PF_6]$ $Ru(\eta\text{-}C_6H_6)Cl_2L$ and $[Ru(\eta\text{-}C_6H_6)(MeCN)_3][PF_6]_2$ undergoes nucleophilic attack by an excess of tertiary phosphines to give η^5-cyclohexadienyl complexes of general formula $[Ru(\eta^5\text{-}C_6H_6PR_3)L_3]^{2+}$ (PR_3 = PMe_3, PMe_2Ph; L_3 = $(PMe_3)_3$; $(PMe_3)_2$, PPh_3; (PMe_3), (PPh_3), PMe_2Ph; $(PMe_3)_2$, $P(NMe_2)$; $P(Me_3)_2$, MeCN)[19] (Equation [3]).

$$[Ru(\eta\text{-}C_6H_6)Cl(PR_3)PR'_3][PF_6] + 2PR''_3 \xrightarrow[-(NH_4Cl)]{NH_4PF_6}$$



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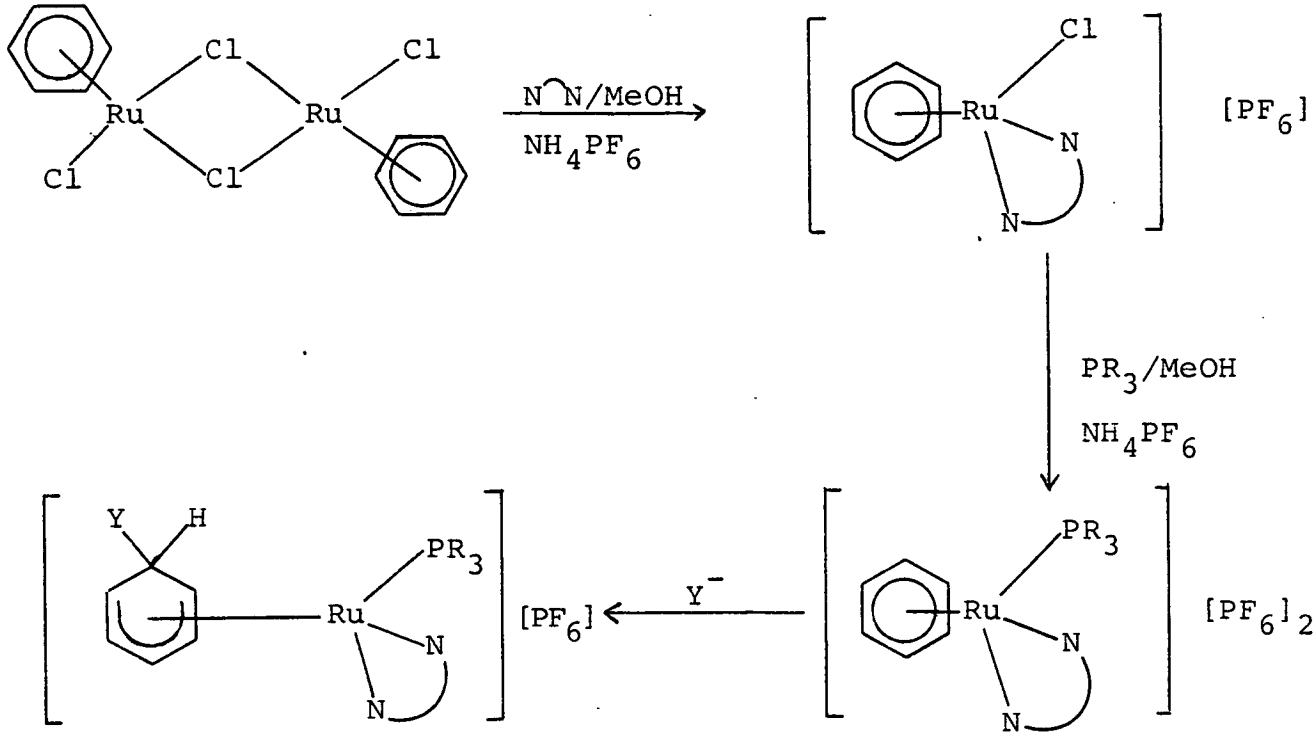
Some mixed amine-phosphine complexes have also been synthesised[13]. These are important in that they react with a wider range of nucleophiles, such as H^-, OH^-, CN^-, to give stable η^5-cyclohexadienyl complexes (Scheme 1.1).

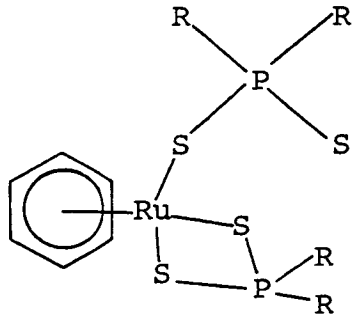
Scheme 1.1 The Synthesis of mixed Amine-Phosphine Complexes and their Reaction with Nucleophiles



(Y = H, OH, CN; N⌒N = 1,10-phenanthroline, 2,2'bipyridyl; PR_3 = PMe_2Ph).

The number of areneruthenium(II) complexes containing sulphur donor ligands is relatively small. The reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ with an excess of aqueous $Na[S_2PR_2]$ (R = Me, OMe, OEt), or its corresponding ammonium salt, gives the monomeric species $Ru(\eta\text{-arene})(S_2PR_2)_2$ [22,23] (5), whereas with $NH_4[S_2PPh_2]$ (in 1:2 mol ratio) the monosubstituted $[Ru(\eta\text{-}C_6H_6)Cl(S_2PPh_2)]$ (6) is formed. The chloride ion may then be displaced with various Lewis bases (L) to form the cationic $[Ru(\eta\text{-}C_6H_6)L(S_2PPh_2)]^+$ (L = PPh_3, PMe_2Ph, $P(OMe)_3$, $SbPh_3$, py, etc.).

The uni- and bidentate dithiophosphate groups in compounds (5) do not undergo interchange on the n.m.r. timescale up to ambient temperature in contrast to the behaviour of their rhodium analogues[22,23], $Rh(\eta^5\text{-}C_5Me_5)(S_2CNMe_2)_2$.



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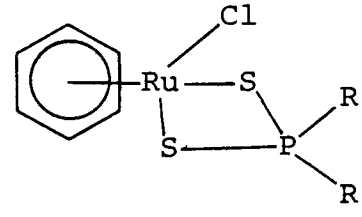


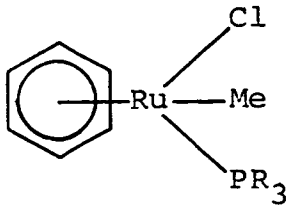
(6)

The stability and range of compounds available is much greater for the pentamethylcyclopentadienyl rhodium system than for the isoelectronic arene ruthenium system. Thus although many rhodium dithiolenes and dithiocarbamates are known, reaction of $^-[S_2CNR_2]$ or $^-[S_2COR]$

with $[Ru(\eta\text{-arene})Cl_2]_2$ results in displacement of the arene ring[24].

A number of areneruthenium(II) complexes containing metal-carbon σ bonds have been described. These have been obtained either by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ in CH_3CN with an excess of dimethyl mercury, or tetramethyltin and subsequent treatment with a tertiary phosphine, to yield complexes of the type $Ru(\eta\text{-}C_6H_6)Cl(Me)PR_3$ (7). Similarly $Ru(\eta\text{-}C_6H_6)Cl(Ph)(PR_3)$ is formed by reaction with diphenyl mercury[25].

The yellow, air-sensitive, dimethyl complexes $Ru(\eta\text{-arene})Me_2(PMe_2Ph)$ are obtained upon addition of excess methyl lithium to the above solutions[5]. Reaction with ethylating reagents has been reported, generally, to lead to decomposition of the arene ruthenium(II) species, possibly <u>via</u> β-elimination and generation of terminal ruthenium hydrides. The stability of these and many other arene ruthenium systems is dependent on the degree of substitution of the arene ring. Thus species in which the arene is hexamethylbenzene are usually of greater stability than those in which the arene has a lower degree of permethylation.



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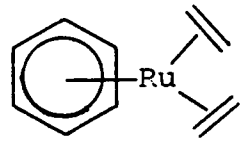
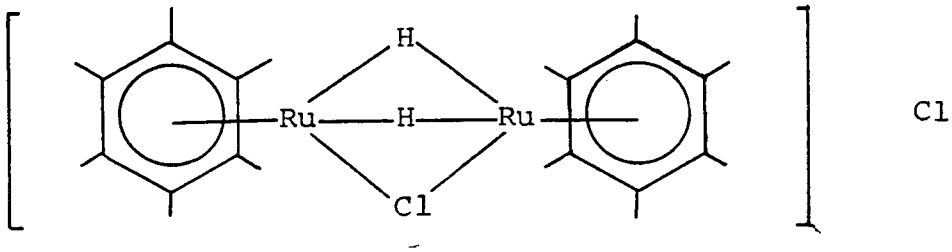


(8)

Several complexes have been reported in which mono-olefins and chelating di-olefins are coordinated to a ruthenium centre. Thus the ruthenium(0) species $Ru(\eta\text{-}C_6H_6)(C_2H_4)_2$ (8) and $Ru(\eta\text{-}C_6H_6)(1,5\text{-}C_8H_{12})$ are prepared from $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ and ethene or 1,5-cyclo-octadiene respectively in the presence of a reducing agent[26]. In the presence of ethanolic sodium carbonate[28], the hexamethylbenzene dimer, $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ reacts with ethylene to form $Ru(\eta\text{-}C_6Me_6)(C_2H_4)_2$ (Equation [4]). The same species has been reported as being formed by reaction of $[Ru_2(\eta\text{-}C_6Me_6)_2Cl(H)_2]Cl$ (9) with ethene in propan-2-ol[29]. However, the synthesis of the di-μ-hydride has recently been reported as being "inexplicably irreproducible"[30].



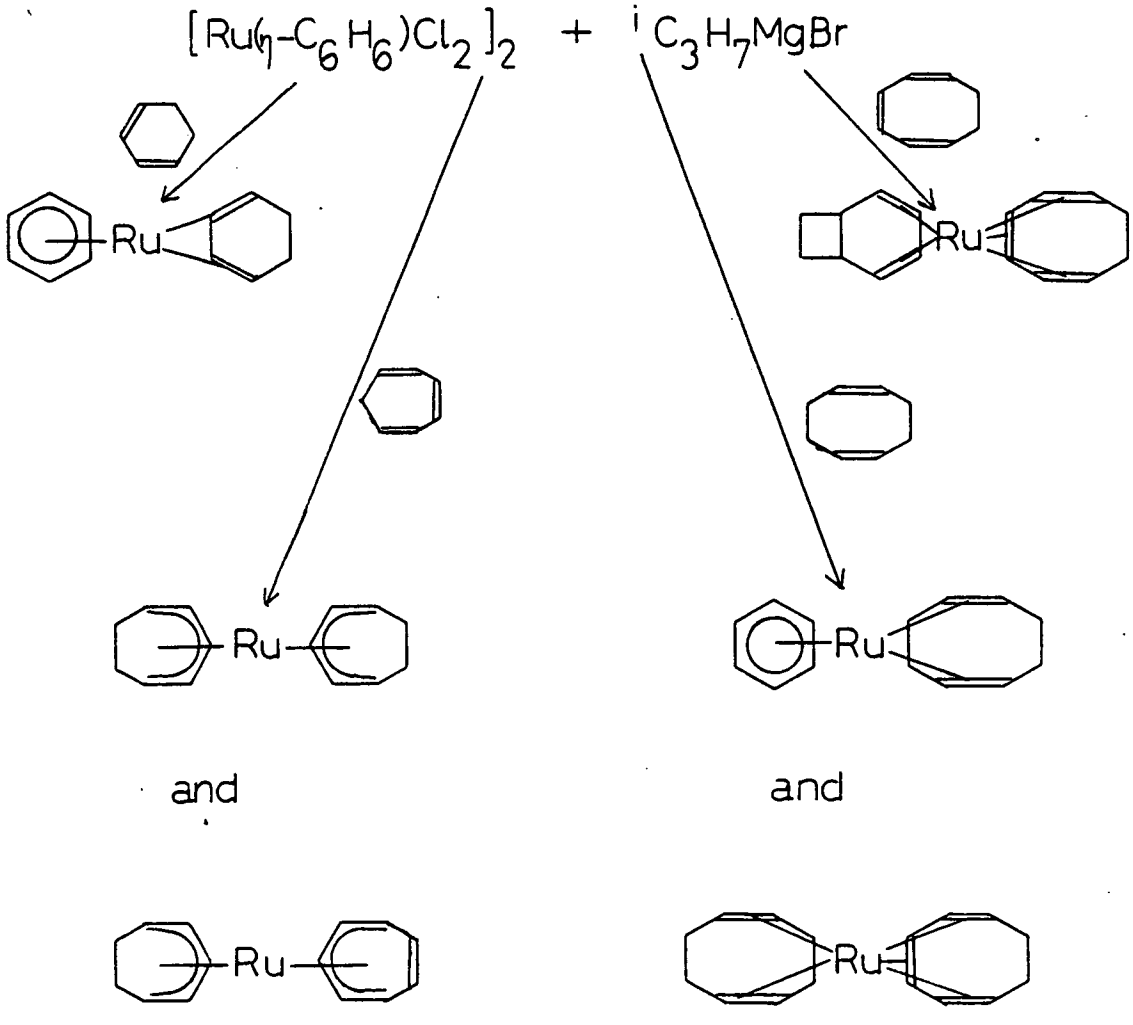
(9)

$$[Ru(\eta\text{-}C_6Me_6)_2Cl_4] + 4\ C_2H_4 + 2\ C_2H_5OH + 2\ Na_2CO_3$$

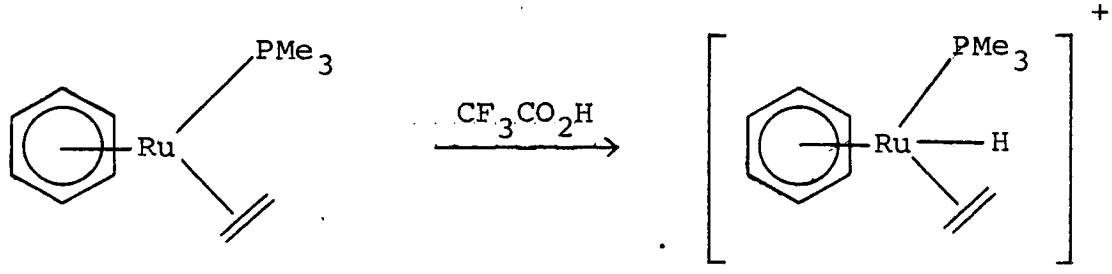
$$\longrightarrow\ 2[Ru(\eta\text{-}C_6Me_6)(C_2H_4)_2] + 2CH_3CO + 4NaCl + 2H_2O + 2CO_2 \quad \ldots\ldots\ [4]$$

In the presence of isopropyl magnesium bromide[27], $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ undergoes a variety of reactions with dienes and trienes (Scheme 1.2). Several of these involve either loss of the coordinated benzene or carbon atom(s) insertion into π-bonded rings.

Scheme 1.2 The reactions of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with Dienes and Trienes



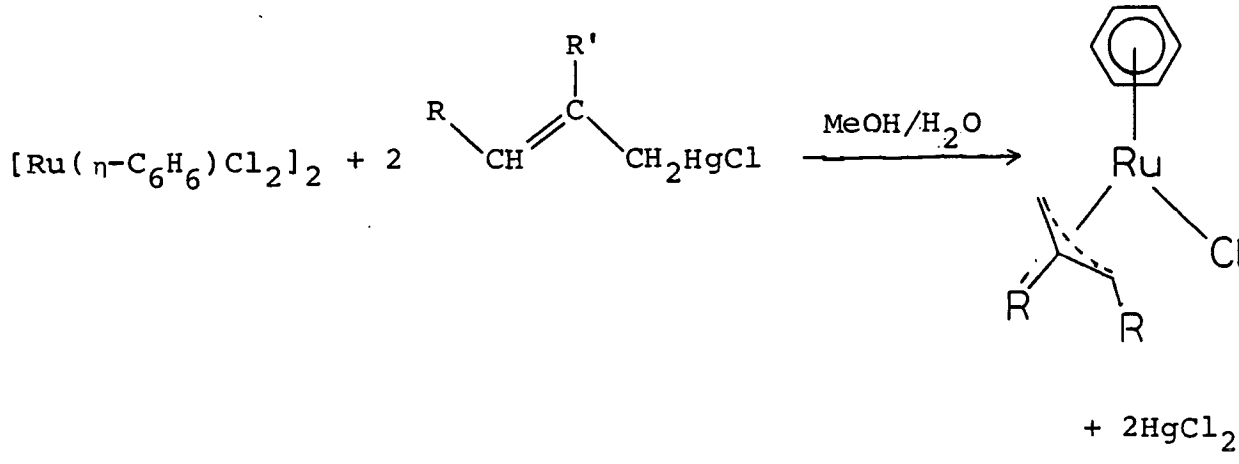
Ruthenium(II) arene-olefin complexes may also be prepared, either directly, e.g. by the reaction of $Ru(\eta\text{-}C_6H_6)(PMe_3)Cl_2$ with $AgPF_6$ and ethene in acetone which gives the cationic ethene complex, $[Ru(\eta\text{-}C_6H_6)(PMe_3)Cl(C_2H_4)]^+$, (this may then be reduced with sodium naphthalide to the zerovalent $Ru(\eta\text{-}C_6H_6)(PMe_3)(C_2H_4)$[31,32] (10)) or from a ruthenium(0) precursor, by oxidation, e.g. by reaction of (10) with trifluoroacetic acid which yields the monocationic terminal hydride (11).



(10) (11)

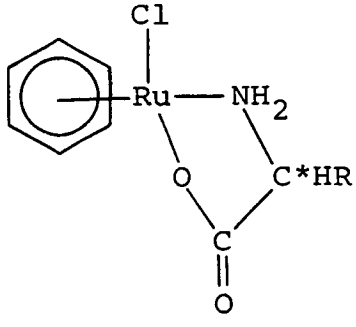
The first areneruthenium(II) complexes containing η^3-allyl groups were reported in 1972[25], when reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with tetraallyltin, in acetonitrile, under mild conditions was shown to give the yellow $Ru(\eta\text{-}C_6H_6)Cl(\eta^3\text{-}C_3H_5)$ in high yield. A much wider range of allyls can be produced by using allylmercuric halides as the allylating agent[33,34] (Scheme 1.3). The nature of the metal-allyl interaction is currently under investigation in this department[35].

Scheme 1.3 The Formation of η^3-allyl Areneruthenium(II) Complexes



(allyl = allyl, 1 and 2-methyl allyl, 1 and 2-phenyl allyl, 1-acetyl-2-methyl allyl).

Several of the classes of compound already discussed contain examples which are chiral. Reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with amino-acid anions gives a series of chiral complexes (12). Solution n.m.r. studies have shown that these species epimerized only slowly at the metal[36].



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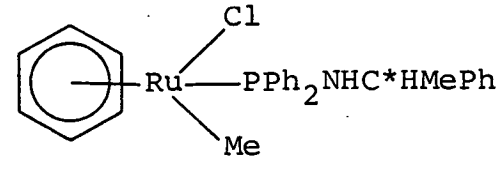
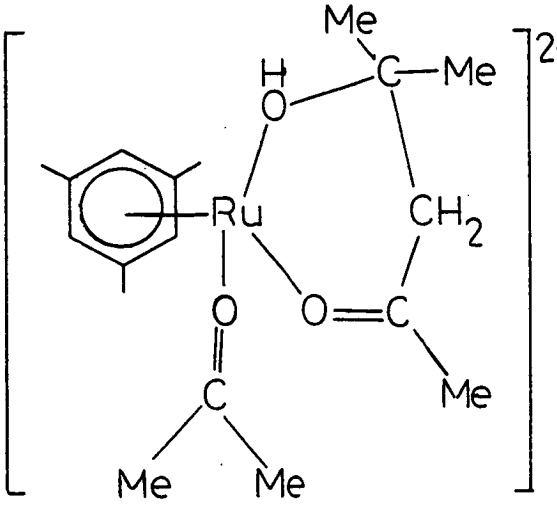


(13)

The optically active species, $Ru(\eta-C_6H_6)Cl(Me)-(PPh_2NHC^*HMePh)$, has been prepared from $[Ru(\eta-C_6H_6)Cl_2]_2$ by reaction with dimethylmercury[25] in acetonitrile and subsequent addition of the optically active phosphine R-(+)-Ph_2PNHC^*HMePh. The diastereoisomers have been separated by a combination of column chromatography and fractional crystallisation. Corresponding diastereomeric $SnCl_3$ complexes $Ru(\eta-C_6H_6)Me(SnCl_3)(PPh_2NHC^*HMePh)$, are obtained by treatment of the chloro complexes with anhydrous $SnCl_2$ [37].

An important feature of $[Ru(\eta-arene)Cl_2]_2$ complexes is that they may be readily converted to ruthenium(II) bis arene complexes, via the synthetically useful trisacetone precursor $[Ru(\eta-arene)(Me_2CO)_3]Y_2$. Maitlis et al[38-41] have reported that the isoelectronic $[M(\eta^5-C_5Me_5)(Me_2CO)_3]Y_2$ (M = Rh, Ir; Y = BF_4, PF_6) may be generated in situ from $[M(\eta-C_5Me_5)Cl_2]_2$ and $Ag[BF_4]$ or $Ag[PF_6]$ in acetone. This work has been extended by Bennett et al[18,42], to the analogous areneruthenium(II) cations and these species may be isolated at 273 K as the $[BF_4]^-$ or $[PF_6]^-$ salts. On warming the $[BF_4]^-$ salt to 298 K, an aldol condensation reaction of the co-ordinated acetone occurs, to give the complexes $[Ru(\eta-arene)(Me_2CO)-\{Me_2C(OH)CH_2COMe\}][BF_4]_2$ (14), containing the bidentate 4-hydroxy-4-methylpentan-2-one ligand. If the anion is $[PF_6]^-$, then the aldol condensation is presumed to be the first step in the partial hydrolysis of that anion. Over a period of several hours the species $[Ru(\eta-arene)(Me_2CO)_3][PF_6]_2$ reacts further to form mesityl oxide, as the major organic

product, and the tri-μ-difluorophosphate complexes $[Ru_2(\eta\text{-arene})_2(\mu\text{-}PO_2F_2)_3][PF_6]$ (arene = C_6H_6, $1,3,5\text{-}C_6H_3Me_3$ C_6Me_6) (15). A similar reaction is reported to occur more slowly with $[Rh(\eta^5\text{-}C_5Me_5)(Me_2CO)_3][PF_6]_2$[38,40] and the formation of $Mn(O_2PF_2)(CO)_5$, from the reaction of $MnCl(CO)_5$ and $Ag[PF_6]$, has also been reported[43].



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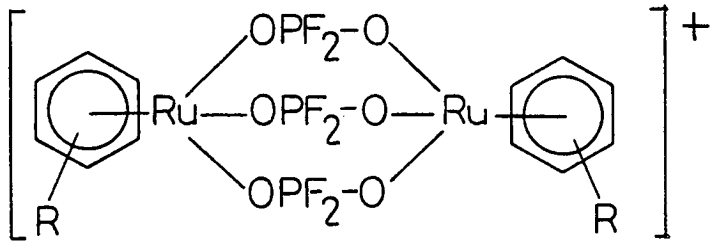


(15)

A wide variety of ruthenium(II) bis arene complexes $[Ru(\eta\text{-arene})(\eta\text{-arené})][Y]_2$ ($Y = BF_4^-$, PF_6^-) have been obtained by <u>in situ</u> treatment of the trisacetone species with a variety of arenes in the presence of acid (CF_3CO_2H, HBF_4 or HPF_6). As has been noted previously, yields (and stability) are increased by using arenes with a high degree of permethylation. The arene may undergo reaction once co-ordinated to the ruthenium(II) centre, e.g. η -chlorobenzene is converted to the anisole complex on addition of methanol. However, unlike the isoelectronic

$[Rh(\eta^5\text{-}C_5Me_5)(\eta^6\text{-arene})]^{2+}$ cations, these coordinated arenes are not readily replaced by other ligands[39,44].

However, it has been shown that the arene groups in some of the complexes described in this Chapter can be replaced by other ligands under thermal or photochemical reaction conditions. Indeed both $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ and $[Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Cl_2]_2$ are best prepared by exchange reactions of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ with an excess of the appropriate ligand at high temperatures[28], rather than by reaction of ethanolic ruthenium trichloride with the appropriate cyclohexadiene.

An extensive study[5] has been made of the relative rates of exchange of p-cymene and benzene in the complexes $Ru(\eta\text{-arene})Cl_2(PBu^n_3)$. In all cases where reaction was observed, the p-cymene ring was found to be more labile. Under the influence of U.V. irradiation even cumene displaced the η-p-cymene ring. However arenes having strong electron-withdrawing substituents, such as Cl, F, CF_3 or CO_2Et failed to displace either of these arenes. Despite its greater lability, crystallographic analysis of the complexes $Ru(\eta\text{-arene})Cl_2(PMe_2Ph)$ (arene = C_6H_6, p-cymene) has shown there to be no significant difference in the metal-ring distances[45], so that the energy difference between the metal-ring bonds in the two complexes is presumably small.

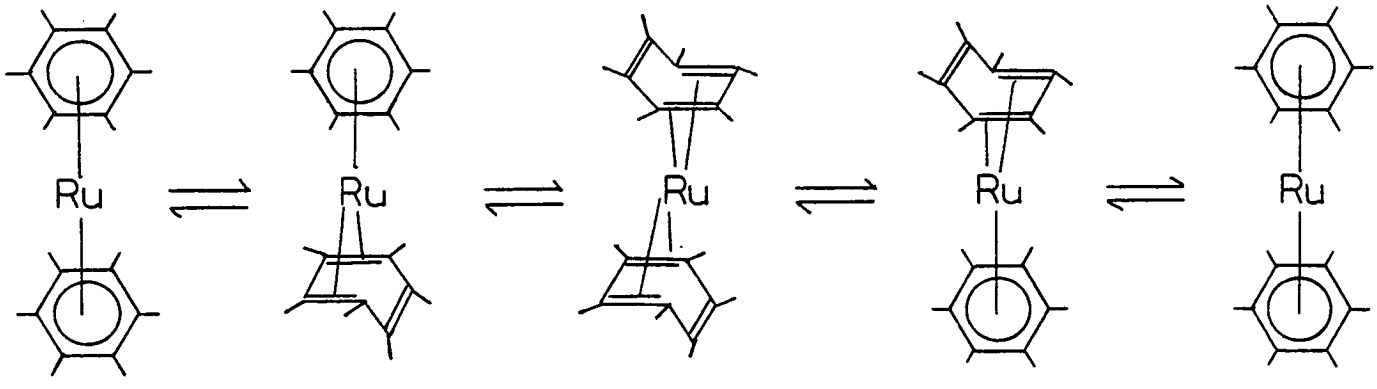
It has recently been reported[46] that the arene in the complex $[Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)][PF_6]$ can be displaced by U.V. irradiation in acetonitrile to form the synthetically useful species $[Ru(\eta^5\text{-}C_5H_5)(CH_3CN)_3][PF_6]$. This complex has been used to synthesise compounds of the type $[Ru(\eta^5\text{-}C_5H_5)L_3][PF_6]$ (L = $P(OMe)_3$; L_3 = hexamethylbenzene, [2.2]-p-cyclophane, p-dichlorobenzene, η^6-cyclooctatetraene). Behaviour of a similar nature has also been reported for the photolysis of the $[Fe(\eta^6\text{-}MeC_6H_4Me)(\eta^5\text{-}C_5H_5)]^+$ cation, in methylene chloride in the presence of potential ligands[47,48].

Although the phenomenon of arene exchange is quite general in transition metal chemistry, the mechanism of exchange in η^6-arene complexes of the types described above has not been fully established, despite extensive investigation[49,50]. It would seem that in the last case discussed a reasonable, intuitive scenario would start with an η^6 to η^4 transformation of the coordinated arene. The coordinatively unsaturated molecule would then undergo attack by a solvent molecule. This intermediate would then undergo a further transformation to a η^2-arene complex, coordinate a second solvent molecule and, finally, the η^2-arene complex would eliminate the arene. Evidence for the initial η^6-η^4 transformation is provided by variable temperature ^1H n.m.r. spectral studies on ruthenium(0)bis(hexamethylbenzene)[51]. At low temperatures (<278 K) four distinct methyl environments are observed; the methyl groups become

equivalent as the temperature is raised (308 K). These results can be interpreted as evidence for an equilibrium between η^6 and η^4 structures (Scheme 1.4). However, in the absence of a suitable solvent, arene exchange in η^6-arene-metal complexes can proceed by either intramolecular or intermolecular dissociative and associative processes.

A dissociative process could involve either complete arene dissociation or ligand dissociation prior to binding a new arene molecule to the metal centre. The dissociative reaction could involve one step or more likely a series of three steps, analogous to the η^6-η^4-η^2 transformation described above (Scheme 1.5).

Scheme 1.4 The Equilibrium between η^6 and η^4 forms of $Ru(C_6Me_6)$



Scheme 1.5 A dissociative mechanism for arene exchange

$$(\eta^6\text{-arene})\,RuL_x \rightleftharpoons \text{arene} + RuL_x$$

$$\text{arene}' + RuL_x \rightleftharpoons (\eta^6\text{-arene}')\,RuL_x$$

(x = 2,3)

Scheme 1.6 A mechanism for arene exchange involving initial ligand (L) loss

$$(\eta^6\text{-arene})\,RuL_x \overset{-(L)}{\rightleftharpoons} (\eta^6\text{-arene})\,(RuL_{x-1})$$

$$(\eta^6\text{-arene})\,(RuL_{x-1}) \overset{\text{arene}'}{\rightleftharpoons} (\eta^6\text{-arene})\,RuL_{x-1}\,(\eta^2\text{-arene}')$$

$$(\eta^6\text{-arene})\,RuL_{x-1}\,(\eta^2\text{-arene}') \rightleftharpoons (\eta^4\text{-arene})\,RuL_{x-1}\,(\eta^4\text{-arene}')$$

$$(\eta^4\text{-arene})\,RuL_{x-1}\,(\eta^4\text{-arene}') \rightleftharpoons (\eta^6\text{-arene}')\,RuL_x \quad (-(\text{arene}),\ +(L))$$

Scheme 1.7 An intramolecular associative mechanism for arene exchange

$$(\eta^6\text{-arene})\,RuL_x + \text{arene}' \rightleftharpoons (\eta^4\text{-arene})\,RuL_x\,(\eta^2\text{-arene}')$$

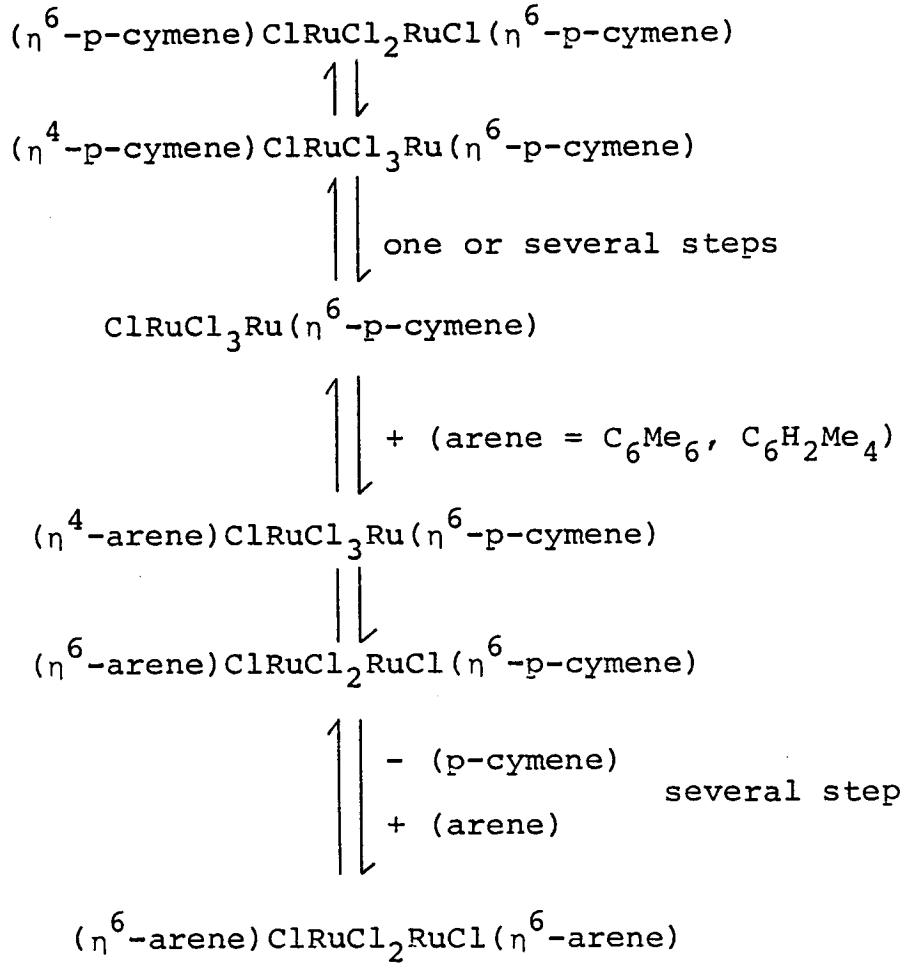
$$(\eta^4\text{-arene})\,RuL_x\,(\eta^2\text{-arene}') \overset{\text{several steps}}{\rightleftharpoons} (\eta^6\text{-arene}')\,RuL_x + \text{arene}$$

As this process would presumably involve a highly reactive ML_x intermediate, perhaps initial dissociation of a ligand (L), to give a 16 electron intermediate, and subsequent attack by arene', would be a more thermodynamically plausible mechanism (Scheme 1.6).

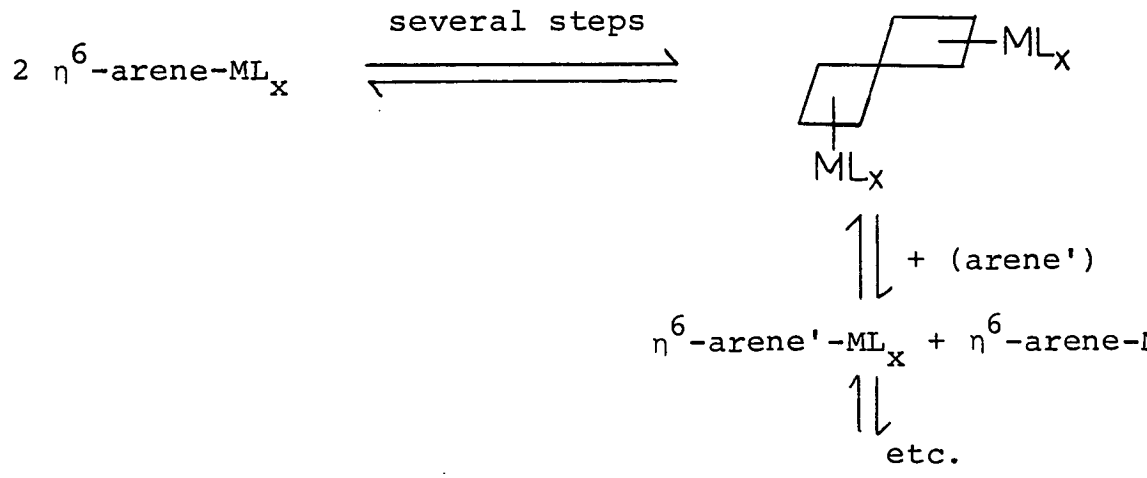
If the process is an intramolecular associative one, then the first step would involve a twenty-electron intermediate or transition state (Scheme 1.7). The first step could involve a preliminary rearrangement of the η^6-arene to an η^4-arene, before coordination of the second arene. If the process is intramolecular, then the relative activation energies for the η^6-arene-metal$\rightleftharpoons\eta^4$-arene-metal step and the ligand dissociation step will determine which mechanism will operate.

High energy intermediates generated by dissociative processes could be stabilised by interaction of the parent arene-ML_x through M-L-M or M-arene-M interactions, with the former probable in complexes where L is an effective bridging ligand, e.g. halide, psuedo-halide or hydride. This type of mechanism would be particularly likely in the case of arene exchange with the complex $[Ru(\eta\text{-p-cymene})Cl_2]_2$, since the two metal centres are already connected. A possible mechanism for exchange is illustrated (Scheme 1.8).

Scheme 1.8 A mechanism for exchange of the complex $[Ru(\eta\text{-p-cymene})Cl_2]_2$



Scheme 1.9 An exchange mechanism involving intermolecular stabilisation



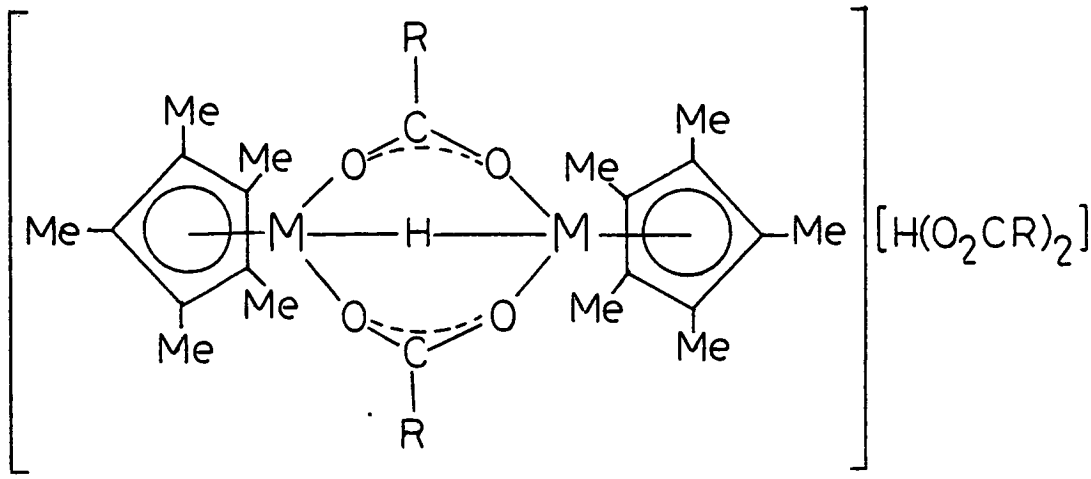
In the second type of intermolecular stabilisation the arene ring could be bound to a second metal site, i.e. one ML_x fragment, could be stabilised by a second molecule arene-ML_x (Scheme 1.9). This type of process might be more likely for exchange reactions of the monomeric species [Ru(η-arene)Cl_2(PBu^n_2)]. There have been several examples quoted in the literature[52,53] in which an arene ring has been found to interact with more than one metal centre.

The evidence for many of the proposed mechanisms is slight, and in particular, the extent to which an η^6-arene is unzipped before exchange occurs, is difficult to determine. Must exchange follow a sequence $\eta^6 \rightleftharpoons \eta^4 \rightleftharpoons \eta^2$ or do η^6-arene $\rightleftharpoons$ free arene, or $\eta^6 \rightleftharpoons \eta^2 \rightleftharpoons$ free arene sequences prevail? A series of extended Huckel molecular orbital calculations[54] have shown that the η^6 to η^4 transformation is of very low energy and hence, it might be expected that several of the reactions described above follow this low energy pathway. Finally, many of the complexes described in this section have important catalytic properties and these will be discussed, together with the catalytic properties of binuclear η -arene ruthenium(II) species, in the introduction to Chapter 2.

1.2 The synthesis of the mononuclear complexes $Ru(\eta\text{-arene})Cl(O_2CR)$ and $Ru(\eta\text{-arene})(O_2CR)_2$

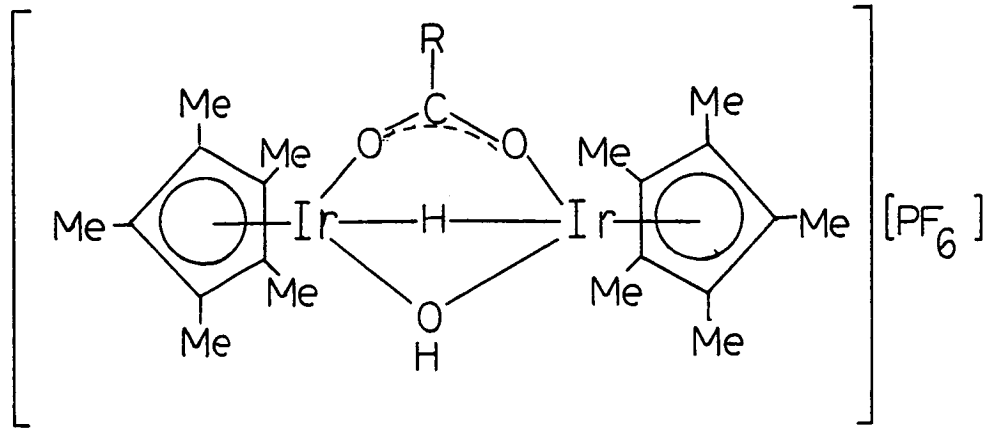
A variety of acetato and trifluoroacetato complexes of pentamethylcyclopentadienyl rhodium(III) and iridium(III) have been reported[57,58]. The work reported in this section describes the extension of these syntheses to the isoelectronic arene ruthenium(II) complexes.

The complexes $[M(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (M = Rh, I) react in dry benzene with silver acetate to give $M(\eta\text{-}C_5Me_5)(O_2CCH_3)_2.H_2O$ and subsequent treatment with trifluoroacetic acid yields the analogous $M(\eta\text{-}C_5Me_5)\text{-}(O_2CCF_3)_2.H_2O$ [37]. Although the rhodium acetato complex is stable, the iridium complex is readily converted by hydrolysis to a hydroxo complex, $Ir(\eta\text{-}C_5Me_5)(OH)_2.4H_2O$. This reaction is however reversible since treatment with acetic acid results in the reformation of $Ir(\eta\text{-}C_5Me_5)(O_2CCH_3)_2\text{-}.H_2O$. These complexes have been shown to be useful precursors for the synthesis of a variety of μ-hydrido bridged complexes[58] Thus, reaction of $M(\eta\text{-}C_5Me_5)(O_2CR)_2.H_2O$ (M = Rh, Ir; R = CH_3, CF_3) with hydrogen in benzene under mild conditions gives the binuclear triple bridged complex $[M_2(\eta\text{-}C_5Me_5)_2(H)(O_2CR)_2][H(O_2CR)_2]$ (16) in which the anion is the proton bridged $[RCO_2...H...O_2CR]^-$.



(16)

Prolonged interaction with hydrogen gave the di-μ-hydrido bridged cation $[M_2(\eta\text{-}C_5Me_5)_2(H)_2(O_2CR)]^+$ in all cases except that of the iridium acetato complex. The interaction of this complex with hydrogen in wet isopropanol gave the mixed bridged species $[Ir_2(\eta\text{-}C_5Me_5)_2(H)(OH)(O_2CCH_3)][PF_6]$ (17) which was also formed by reaction of (16) (M = Ir, R = CH_3) in aqueous acetone.



(17)

Finally, the iridium complex, $[Ir_2(\eta\text{-}C_5Me_5)_2(H)_2(O_2CCF_3)][H(O_2CCF_3)]$ undergoes further hydrogenation in the presence of triethylamine to give the tri-μ-hydrido cation $[Ir_2(\eta\text{-}C_5Me_5)_2(H)_3]^+$ which can be isolated as its hexafluorophosphate salt. The same complex is also formed by the hydrogenation of $[Ir(\eta\text{-}C_5Me_5)Cl_2]_2$ in isopropanol and aqueous acetone.

The reaction of $M(\eta\text{-}C_5Me_5)Cl_2(PMe_3)$ with silver acetate gave the complexes $M(\eta\text{-}C_5Me_5)(O_2CMe)_2(PMe_3)$ which contain unidentate carboxylate groups[59], and treatment of these with aqueous $K[PF_6]$ produced $[M(\eta\text{-}C_5Me_5)(O_2CMe)(PMe_3)][PF_6]$ in which the carboxylate is symmetrically coordinated.

Several η-hexamethylbenzene ruthenium(II) carboxylate complexes have recently been reported in the literature while the work described in this chapter was in progress. The complex $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ [60] is obtained by essentially the same route in this chapter, whereas $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PMe_3)$ and $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)(PMe_3)][PF_6]$ were obtained from $Ru(\eta\text{-}C_6Me_6)Cl_2(PMe_3)$ in a manner analogous to that for the rhodium and iridium pentamethylcyclopentadienyl complexes described above. The trifluoroacetato complexes $Ru(\eta\text{-}C_6Me_6)(Me)(O_2CCF_3)(PR_3)$ and $Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PR_3)$ (PR_3 = PMe_3, $PMePh_2$, PPh_3) were obtained by the stepwise cleavage of the metal-carbon bonds in the complexes $Ru(\eta C_6Me_6)(Me)_2(PR_3)$ with trifluoroacetic acid[61]. The complexes $Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PR_3)$ react with an excess of trimethylphosphine, in the presence of

ammonium hexafluorophosphate, to give $[Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)(PMe_3)][PF_6]$, which on treatment with $Na[AlH_2(OC_2H_4OMe)_2]$ give the stable dihydrides, $Ru(\eta\text{-}C_6Me_6)(PR_3)(H)_2$.

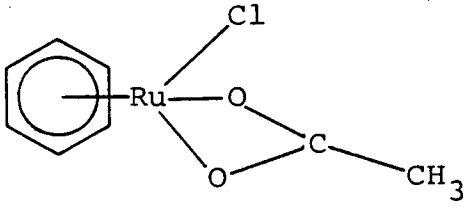
The work reported in this first section has been carried out by ourselves and in collaboration with Dr. M.A. Bennett and co-workers at the Australian National University, Canberra.

Three synthetic strategies have been investigated in our attempts to prepare complexes of the general formula $Ru(\eta\text{-arene})X(O_2CR)$ (X = Cl, Br; R = Me, CF_3; arene = C_6H_6; 1,3,5-$C_6H_3Me_3$, 1,4-$MeC_6H_4CHMe_2$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6) (not all possible combinations) from the corresponding dihalides $[Ru(\eta\text{-arene})X_2]_2$. Not all the complexes were successfully synthesised by all three routes. Thus (i) reaction of $[Ru(\eta\text{-arene})X_2]_2$ with mixtures of the carboxylic acid and its acid anhydride works well when arene = C_6H_6 or 1,4-$MeC_6H_4CHMe_2$ X = Cl and R = Me; and also for arene = C_6H_6 when X = Cl, Br, I and R = CF_3.

While (ii) the reaction of the arenedichlororuthenium(II) dimer $[Ru(\eta\text{-arene})Cl_2]_2$ with an excess of sodium acetate in acetone at room temperature also gives $Ru(\eta\text{-arene})Cl(O_2CCH_3)$ (arene = 1,4-$MeC_6H_4CHMe_2$, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6).

Finally (iii) involves treatment of $[Ru(\eta\text{-arene})X_2]_2$ with two moles of silver carboxylate per mole of dimer in benzene (arene = C_6Me_6; X = Cl; R = Me; arene = C_6Me_6, 1,2,4,5-$C_6H_2Me_4$, 1,3,5-$C_6H_3Me_3$, 1,4-$MeC_6H_4CHMe_2$; X = Br; R = Me).

The reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with acetic acid in the presence of acetic anhydride under reflux for a period in excess of six hours gives a red-brown solution which on cooling deposits the product as a dark red-brown crystalline solid. The solid is initially non-conducting in a variety of solvents and shows only two singlets in its ^1H n.m.r. spectrum, at δ5.76, due to the π-bonded benzene, and at δ1.87 ppm, due to the acetate ligand, in the ratio of 2:1. The infrared spectrum contains bands at 1510 cm^{-1} and 1470-1410 cm^{-1} corresponding to the asymmetric and symmetric ν(OCO) stretching frequencies respectively. The small separation between these bands implies that the acetate is symmetrically coordinated. This spectroscopic evidence and the micro-analytical data are consistent with the formulation of the product as $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$ (18) and the monomeric nature of the complex was confirmed by osmometric molecular weight measurements in acetone (see Experimental, Table 1.1). The structure is presumably analogous to that of the corresponding dithiophosphate compounds[22].



(18)

Note that it is important to use $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ which has been prepared from "purified ruthenium trichloride" i.e. that from which the HCl has been removed by repeated evaporation of its aqueous solution to dryness. If this is not done the reaction proceeds very slowly and the yield of $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$ is greatly reduced. This complex can also be prepared by use of the more soluble 2,4-pentadionato complex, $Ru(\eta\text{-}C_6H_6)Cl(acac)$, in place of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$, and although the reaction is still slow, the yields are much improved. This method also works well for $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ but the corresponding bromo and iodo complexes could not be prepared by this route, because of the insolubility of the precursors in this reaction medium.

The reaction of $[Ru(\eta\text{-}C_6H_6)X_2]_2$ (X = Cl, Br, I) with mixtures of trifluoroacetic acid/anhydride proceeds similarly to give the corresponding $Ru(\eta\text{-}C_6H_6)X(O_2CCF_3)$.

The reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ with sodium acetate in acetone works well for the methylated arenes listed previously. However if arene = C_6H_6 then it has not been possible to obtain $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$ in a pure state, owing to the difficulty of separating this compound from the excess of sodium acetate. Furthermore, although the chloro-acetato complexes have been obtained in good yield it has not been possible to prepare the corresponding bromo-acetato complexes, $Ru(\eta\text{-arene})Br(O_2CMe)$, or the

chloro-trifluoroacetato complexes, $Ru(\eta\text{-arene})Cl(O_2CCF_3)$, using this synthetic route.

Treatment of $[Ru(\eta\text{-}C_6H_6)X_2]_2$ with two moles of silver carboxylate per mole of dimer has proved to be the most versatile of the synthetic strategies investigated, but even this method has its shortcomings. For example, it is unsatisfactory for the chloro-carboxylato complexes of the η-benzene and mesitylene dimers, where a mixture of products, some of which may be binuclear, were obtained.

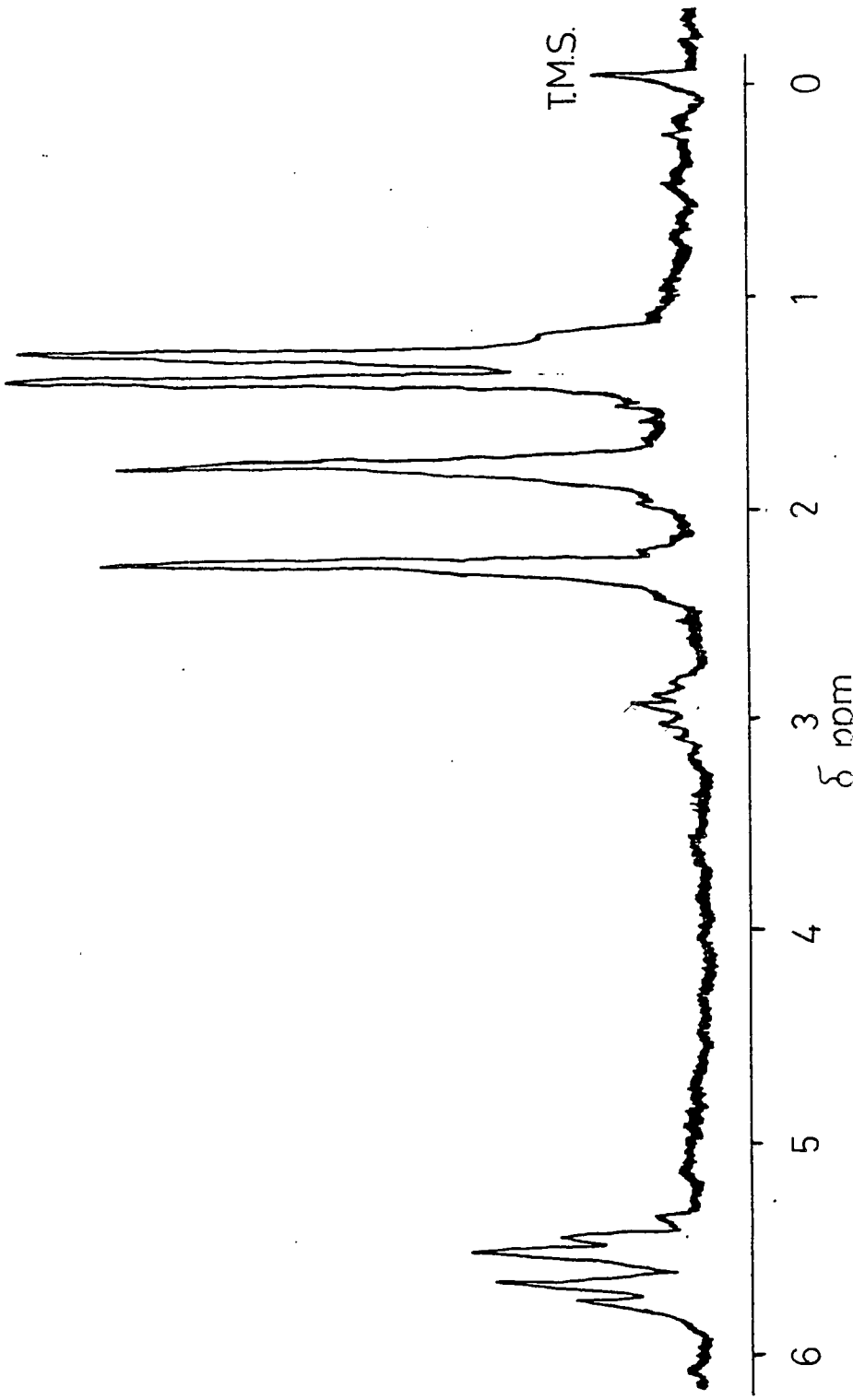
The acetato complexes are readily soluble in water, alcohols and acetone. Those containing methyl-substituted arenes are also readily soluble in dichloromethane and chloroform, though the benzene complex $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$ is generally less soluble in these solvents. The trifluoro-acetates are less soluble than the acetates in all organic solvents and the η-benzene complex, $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$, dissolves readily only in nitromethane. The corresponding bromo and iodo species are for all effective purposes insoluble. Osmometric molecular weight determinations on selected compounds confirm that, with the one exception discussed below, all the complexes are monomeric (Table 1.1). The infrared spectra of the acetate complexes all show a strong band between 1500-1515 cm^{-1} attributed to $\nu_{asym}(OCO)$ and bands at 1470 cm^{-1} and 1410-1420 cm^{-1}, both of which are in the expected region for $\nu_{sym}(OCO)$ (Table 1.2)[62-64]. The methyl deformation mode of the acetate ion lies in the same region as the latter vibration, but irrespective of the correct assignment of these bands, the value of $\Delta\nu[\nu_{asym}(OCO)-\nu_{sym}(OCO)]$ is less than

200 cm^{-1}, and is consistent with the presence of a bidentate acetate group. In the corresponding trifluoroacetate compounds the carboxylate asymmetric stretching frequencies lie in the range 1690-1720 cm^{-1} while the symmetric stretches are located at ca. 1420 cm^{-1}, and these compounds probably have a similar structure. The ^{1}H n.m.r. spectra of the acetato complexes show sharp singlets due to the acetate methyl groups and the expected resonances due to the η-arene, (Table 1.3), a typical example of which is shown in Figure 1.1.

In solvents of high dielectric constant such as methanol or nitromethane there is evidence in both the n.m.r. spectra and from conductivity measurements for slow, but significantly ionic dissociation (Equation [5]). Thus in the ^{19}F n.m.r. spectrum of a freshly prepared d^3-nitromethane solution the singlet, at -75.95 ppm, due to the bound trifluoroacetate ligand of the complex $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$, is partially replaced on standing by a signal at -77.48 ppm, which is ascribed to free $[CF_3CO_2]^-$.

$$[Ru(\eta\text{-arene})Cl(O_2CR)] \underset{+RCO_2^-}{\overset{+solvent}{\rightleftharpoons}} [Ru(\eta\text{-arene})Cl(solvent)_2]^+ + RCO_2^- \quad \ldots\ldots\ldots [5]$$

Figure 1.1 The ^{1}H n.m.r. spectrum of $Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)$ in $CDCl_3$ at 297 K



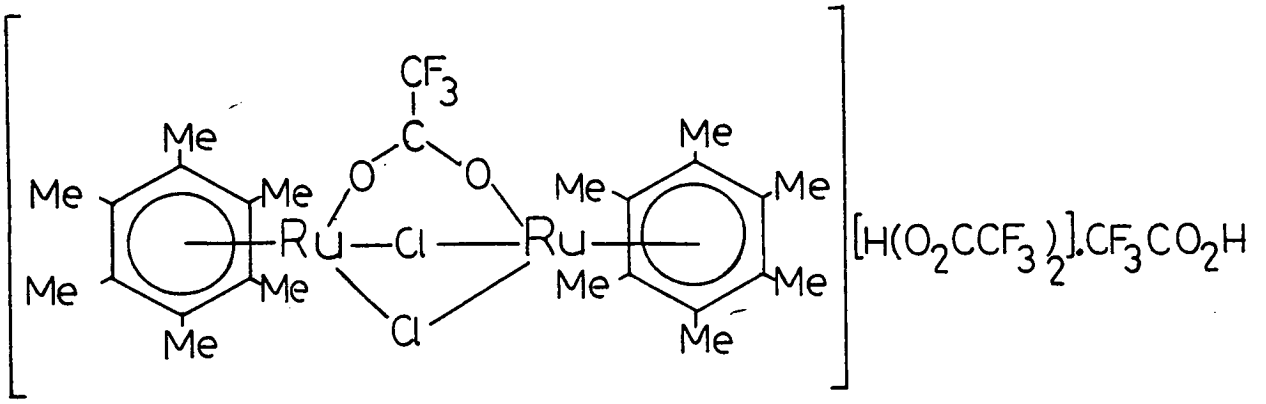
Over a period of time the conductivity of ca. 10^{-3} M solution of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ in nitromethane at 298 K increases from 4.5 $Scm^2\ mol^{-1}$ initially to a steady value of 13.5 $S\,cm^2\ mol^{-1}$ after six hours. Since Λ_m for a 1:1 electrolyte in nitromethane is in the range 60-115 $Scm^2\ mol^{-1}$ (65) this indicates approximately 15-20% dissociation. The behaviour of the acetato complex, $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$, is similar. Thus, the ^1H n.m.r. spectrum of the complex in d^3-nitromethane initially shows singlets at δ5.70 and 1.56 ppm due to the η-benzene and acetate methyl groups respectively. On recording the spectrum again after an interval of 48 hours, an additional peak at 2.02 ppm attributed to free acetate is observed, and the η-benzene resonance is broadened. Over this period an essentially non-conducting ca. 10^{-3} M solution of the complex in nitromethane undergoes the dissociative process discussed above to give a solution which exhibits significant conductivity, ca. 10 $Scm^2\ mol^{-1}$.

The hexamethylbenzene complex $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ behaves differently from its benzene and mesitylene analogues on reaction with trifluoroacetic acid. The product obtained, upon addition of diethyl ether to the residual oil, after removal of the solvent, is a yellow microcrystalline solid of empirical formula $Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3).CF_3CO_2H$. Molecular weight measurements in

dichloromethane indicate that the compound is binuclear, but dilute solutions of the species in nitromethane were appreciably conducting. Assuming a binuclear formulation conductance values of 76-106 $S cm^2$ $equiv^{-1}$ were found for concentrations between 1.0×10^{-3} to 1.25×10^{-4} M. However, although individual values were consistent with the presence of a 1:1 electrolyte, the curvature of the Λ_m vs $C^{\frac{1}{2}}$ Onsager plot suggests the presence of either a higher electrolyte type and/or extensive ion pairing, which may be more probable. The infrared spectrum of the complex contains a strong band at 1782 cm^{-1} which was assigned to the ν_{CO} vibration of the ion $[H(O_2CCF_3)_2]^-$ (cf. $K[H(O_2CCF_3)_2]$, ν_{CO} 1972 cm^{-1} [66]; CF_3CO_2H, ν_{CO} 1819 cm^{-1} [67]). The presence of this proton bridged anion has been reported for the isoelectronic pentamethylcyclopentadienyl rhodium and iridium complexes[58]. Lower frequency bands at 1720, 1648 cm^{-1} and 1445-1385 cm^{-1} have been assigned to the asymmetric and symmetric stretching frequencies respectively of the coordinated trifluoroacetate group.

The ^{19}F n.m.r. spectrum in $CDCl_3$ contains a sharp singlet at δ-76.28 ppm and a very broad resonance at ca. -75.6 ppm in an intensity ratio of ca. 1:2. These peaks can be assigned to the coordinated and hydrogen-bonded trifluoroacetate groups respectively; however no signal in the range 0-20 ppm which could be attributed to the acidic proton was observed. The addition of $Na[PF_6]$ or $Na[BPh_4]$ to a methanolic solution of the compound produced yellow precipitates. Elemental analysis on these

solids were not entirely satisfactory and their ^{1}H n.m.r. spectra sometimes showed more than one resonance in the η-C_6Me_6 region. However, the ^{19}F n.m.r. spectrum of the $[PF_6]^-$ salt showed only the sharp singlet due to the coordinated trifluoroacetate ligand at -76.22 ppm in addition to the usual $[PF_6]^-$ doublet. The broad resonance at -75.6 ppm, due to the $[H(O_2CCF_3)_2]^-$ anion, had disappeared. On the basis of this evidence it is possible to formulate the species formed initially as the binuclear complex $[(\eta\text{-}C_6Me_6)Ru(Cl)_2(O_2CCF_3)Ru(\eta\text{-}C_6Me_6)][H(O_2CCF_3)_2].CF_3CO_2H$ (19), which contains two chloride and one trifluoroacetate bridging ligand. Dissolution of this complex in methanol may facilitate bridge scrambling such that the species trapped out by $[BPh_4]^-$ could be a mixture of complexes containing the bridging units $-Ru(\mu\text{-}Cl)_3Ru-$, $-Ru(\mu\text{-}Cl)_2(\mu\text{-}O_2CCF_3)Ru-$, $-Ru(\mu\text{-}Cl)(\mu\text{-}O_2CCF_3)_2Ru-$ and $-Ru(\mu\text{-}O_2CCF_3)_3Ru-$. Such facile scrambling processes have been found to be quite general in this area of ruthenium(II) chemistry and the results of further studies on this phenomenon are reported in Chapter 2. Further support for these conclusions come from the observation that the complex obtained by reaction of $Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$ with trifluoroacetic acid exhibits identical properties to these described above.

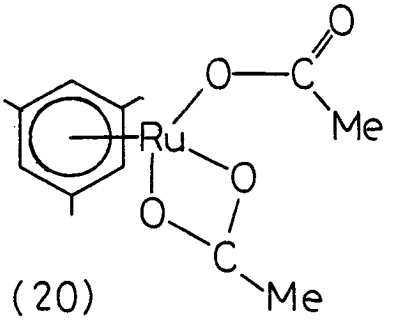


(19)

However, the product which might have been expected from the reaction described above i.e. $Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$ was in fact obtained by treatment of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ with a stoichiometric amount of silver trifluoroacetate.

The reaction of these η-arene ruthenium dimers can be readily extended to give species from which all the chloride ligands have been removed. Thus treatment of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6) with four moles of silver acetate per mole of dimer in benzene at room temperature gives the orange, microcrystalline bis-acetato complexes $Ru(\eta\text{-arene})(O_2CMe)_2$ in good yield. Osmometric molecular weight measurements show the complexes to be monomeric in dichloromethane. The η-durene and hexamethylbenzene complexes were obtained as monohydrates, $Ru(\eta\text{-arene})(O_2CMe)_2.H_2O$, as demonstrated by complete elemental analysis of the latter and by the presence of a peak at 4.30 ppm (due to water) in its ^1H n.m.r. spectrum at 298 K. As mentioned earlier this C_6Me_6 complex has recently been reported in the literature by other workers[60],

who observed a water peak at $\delta 2.70$ ppm in the ^1H n.m.r. spectrum in d^6-acetone. In contrast to this it would appear that the benzene, p-cymene and mesitylene complexes are anhydrous. The infrared spectrum of the complex $Ru(\eta\text{-}C_6H_3Me_3)(O_2CMe)_2$ (20) shows bands at 1620 cm^{-1}, attributed to $\nu_{asym}(OCO)$ (unidentate) 1570 cm^{-1} $\nu_{asym}(OCO)$ (bidentate) 1470 cm^{-1}, $\nu_{sym}(OCO)$ (bidentate); and 1310-1365 cm^{-1}, $\nu_{sym}(OCO)$ (unidentate), thus indicating that the acetate ligands are present in both uni- and bi-dentate binding modes and hence the structure is likely to be that shown below.



(20)

It is probable that the η-hexamethylbenzene and durene complexes also have this structure, although in the infrared spectrum of these species the highest frequency band, due to $\nu_{asy}(OCO)$, is only at 1565 cm^{-1}, perhaps as a consequence of some hydrogen-bonding of the water molecule to the unidentate acetate group. A band at ca. 390 cm^{-1} in the infrared spectrum of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ and $Ru(\eta\text{-}C_6H_3Me_3)(O_2CMe)_2$ can be tentatively assigned to $\bar{\nu}$(Ru-OCOMe)(unidentate) since it is absent from the spectra of the corresponding chloro- and bromo-acetates (Table 1.4). Both the mono- and bis-acetates show strong absorptions at ca. 300 cm^{-1}, which may be due to ν(Ru-OCOMe)(bidentate);

in the case of the chloro-acetates this band is partially obscured by the terminal ν(Ru-Cl) stretch. It was not possible to assign the corresponding ν(Ru-Br) with any degree of certainty.

Treatment of the bis(acetates) with trifluoroacetic acid gives the corresponding bis(trifluoroacetates), isolated as their monohydrates, $Ru(\eta\text{-arene})(O_2CCF_3)_2.H_2O$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, 1,3,5-$C_6H_3Me_3$, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6). The η-benzene complex can also be synthesised by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with four moles of silver trifluoroacetate. However, treatment of the other dimers under comparable conditions generally does not give pure products. The assignment of the ν(OCO) bands in the infra-red spectra of these complexes is ambiguous, although it would appear that both unidentate and bidentate trifluoro-acetate groups are present, and hence it seems probable that the structure is that illustrated previously. The ^1H n.m.r. spectra of these complexes all contain broad bands at ca. 6 ppm which are assigned to the water protons.

As mentioned earlier the complexes $Ru(\eta\text{-arene})(S\text{-}S)_2$ (S-S = S_2PMe_2, S_2PPh_2, $S_2P(OEt)_2$) contain both unidentate and bidentate dithioacid ligands which do not undergo rapid intramolecular exchange on the n.m.r. time scale at room temperature, although the closely related complexes $Rh(\eta\text{-}C_5Me_5)(S\text{-}S)_2$ (S-S = S_2PMe_2, S_2PPh_2, S_2CNMe_2, S_2COEt) do so above room temperature. The ^1H n.m.r. spectra of the bis(acetato) complexes only show one acetate methyl resonance at room temperature, but the change in the ^1H n.m.r. spectrum of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ in $CDCl_3$ between 298 K and 208 K

suggests that another process must be occuring instead of, or in addition to, intramolecular scrambling of the acetate groups (Figure 1.2). On cooling, the peaks at δ2.00 and 2.18 ppm, due respectively to the acetate and arene methyl groups, broaden and apparently coalesce at ca. 223 K. At still lower temperature two new peaks grow on either side of the η-C_6Me_6 resonance. The $^{13}C\{^1H\}$ n.m.r. spectrum shows three peaks at room temperature {δ(ppm) 88.30, $\underline{C}_6(CH_3)_6$; 15.71, $C_6(\underline{C}H_3)_6$; 24.30, $O_2C\underline{C}H_3$} but at 208 K additional peaks are observed at δ87.46, 16.18 and 23.88 ppm (Figure 1.3). These phènomena have been ascribed to a temperature-dependent equilibrium similar to that already discussed for the chloro-acetates, involving either the solvent or the water of hydration (Scheme 1.10). The latter is perhaps the more probable as the water peak in the ^1H n.m.r. at ca. 6 ppm at 298 K, is observed to shift to ca. 9 ppm on cooling.

Scheme 1.10 The temperature dependent equilibration of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$

$$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O \rightleftharpoons [Ru(\eta\text{-}C_6Me_6)(O_2CMe)(solvent)]^+ + [O_2CMe]^-$$

and/or

$$Ru(\eta\text{-}C_6Me_6)(\eta^1\text{-}O_2CMe)(\eta^2\text{-}O_2CMe).H_2O \rightleftharpoons Ru(\eta\text{-}C_6Me_6)(\eta^1O_2CMe)_2(H_2O$$

Figure 1.2 The Variable Temperature ^{1}H n.m.r. spectra of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ in $CDCl_3$ between 298 - 208 K.

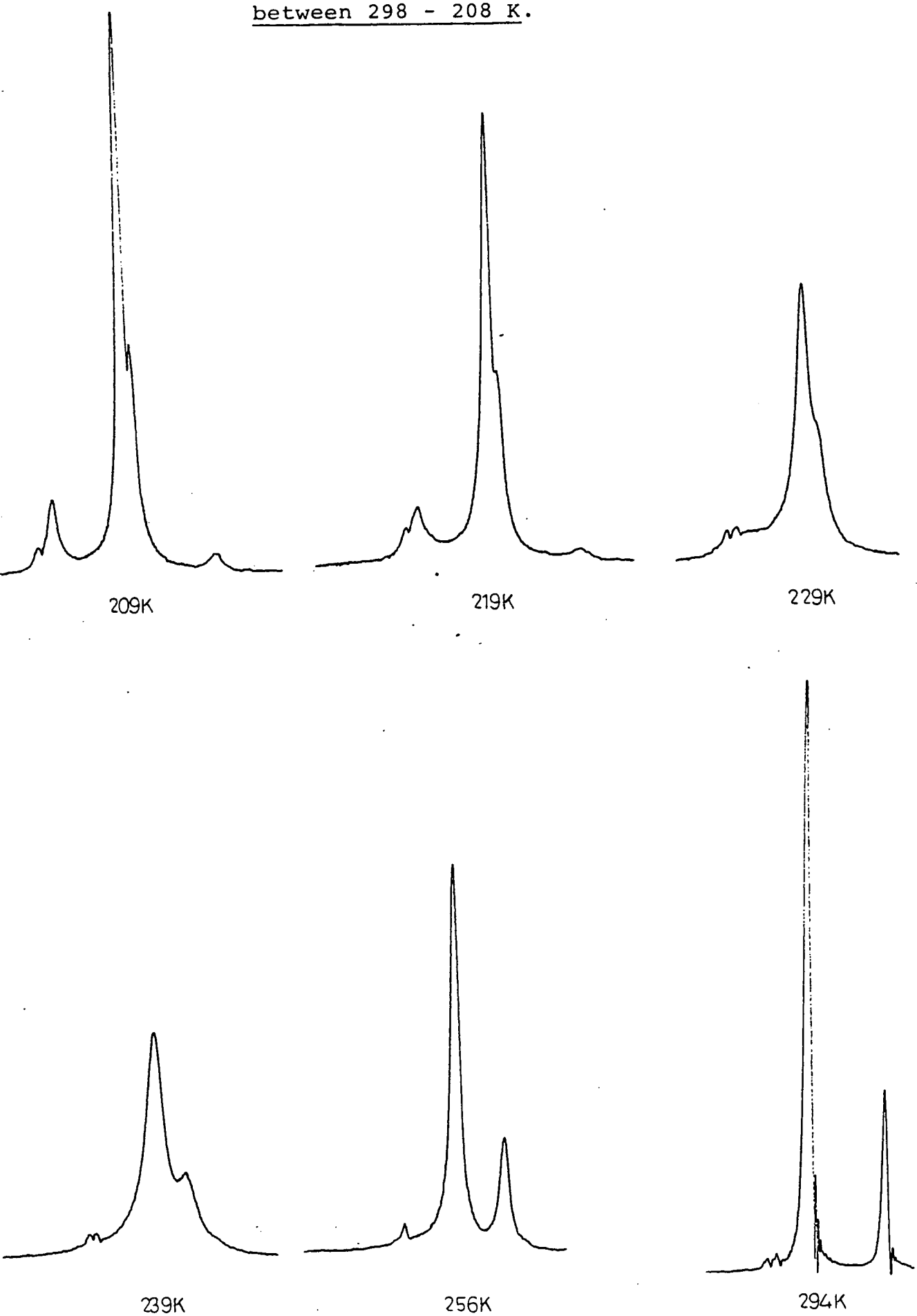
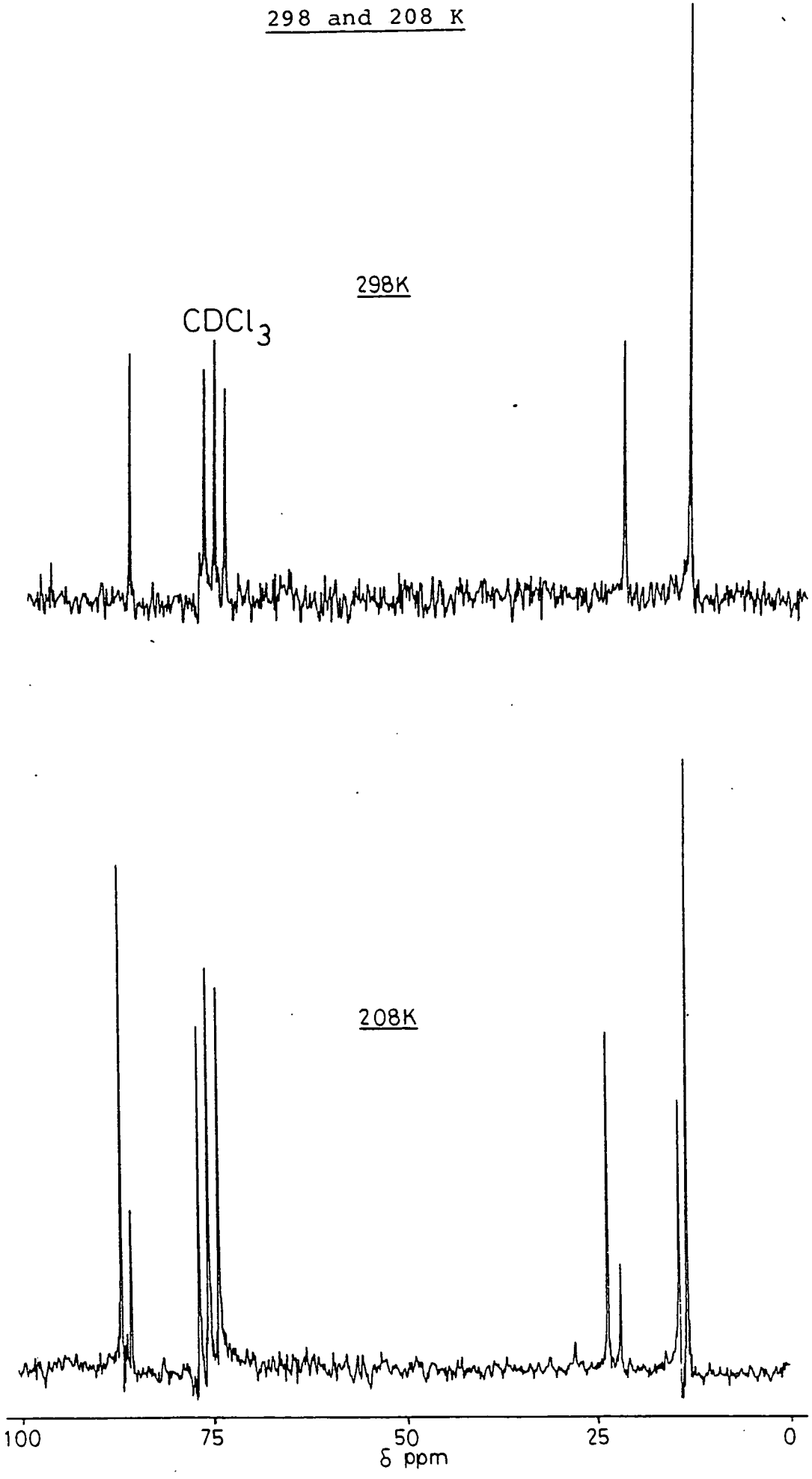


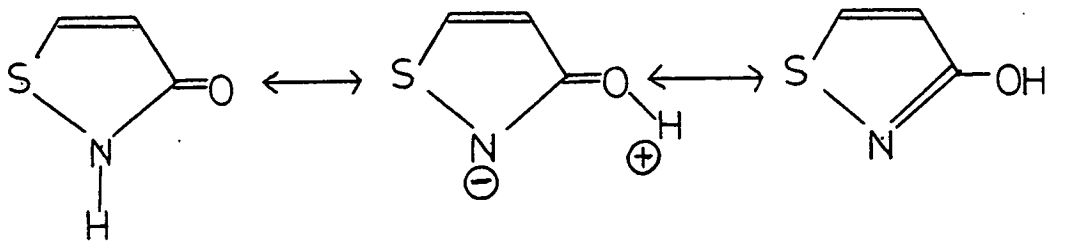
Figure 1.3 The $^{13}C\{^1H\}$ n.m.r. spectra of $Ru(\eta\text{-}C_6Me_2)(O_2CMe)_2.H_2O$ in $CDCl_3$ at 298 and 208 K



The ^{19}F n.m.r. spectrum of $Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$ in CD_3CN shows a sharp singlet at -74.71 ppm due to the trifluoroacetate groups, which are equivalent on the n.m.r. timescale; there are two other weak peaks which may be due to the free $[CF_3CO_2]^-$ ion and the $[Ru(\eta\text{-}C_6H_6)(O_2CCF_3)(CD_3CN)]^+$ cation, but the spectrum remains unchanged on cooling to 243 K.

Attempts to extend the range of compounds available by reaction of the η-arene ruthenium(II) dimers with other acids in methanol were unsuccessful. For example, the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of benzoic acid in methanol gives an orange solution and addition of $Na[BPh_4]$ precipitates an orange solid. The ^1H n.m.r. spectrum of the product in CD_3NO_2 contains a singlet at 5.92 ppm, due to η-benzene, and phenyl resonances at 6.8-7.6 ppm, ascribed to the $[BPh_4]^-$ anion, in the ratio of 12:20. However the infrared spectrum did not contain any bands due to the carboxylate function, although a band at 260 cm^{-1} was assigned to ν(Ru-Cl)(bridging). On the basis of the spectroscopic and microanalytical data, the product was formulated as the well-known compound $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$.

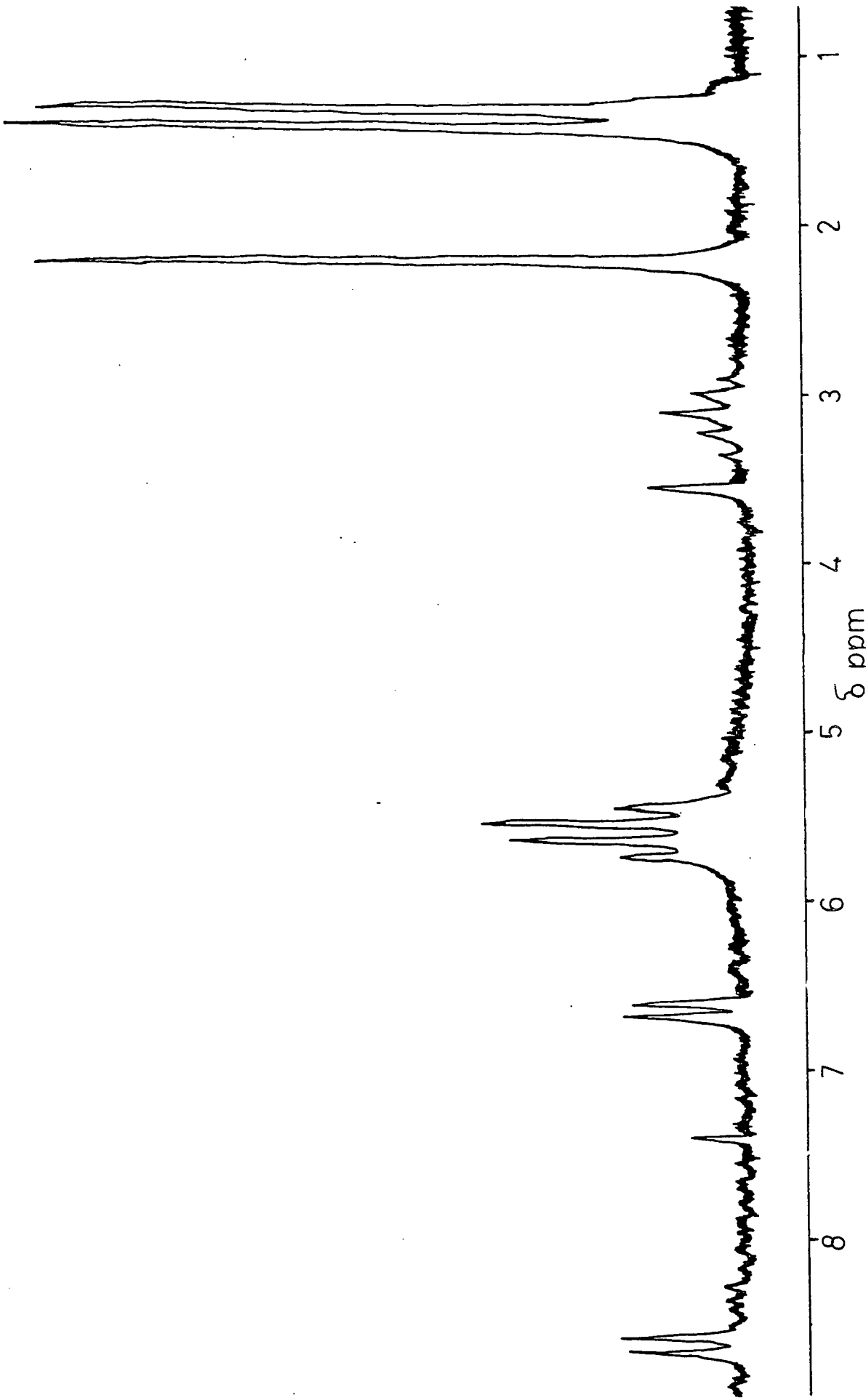
The reaction of the isothiazoline molecule (21a) with $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) in methanol was examined. This molecule is potentially a bidentate ligand, isoelectronic with acetate and the dithioacids. However it can exist in several canonical forms (21b, 21c) and may act as a Lewis base while in (21c). It was hoped that under the conditions employed the ligand would coordinate in the former mode.



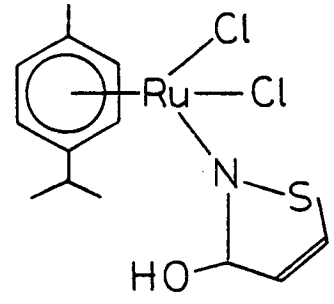
(21a) (21b) (21c)

Treatment of the orange solution, obtained upon reacion of the metal complex $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ with an excess of the ligand, with diethyl ether gave the product as a non-conducting microcrystalline orange solid. Micro-analytical data (Table 1.1) showed that the product contained less nitrogen and more chloride than would have been predicted for a product of the formulation $Ru(\eta\text{-}MeC_6H_4CHMe_2)\text{-}Cl(\eta^2\text{-}NCOC_2H_2S)$. The infrared spectrum of the product showed a broad ν(O-H) at 3550 cm^{-1} and ν(Ru-Cl)(terminal) at 287 cm^{-1}. There were no peaks present which could be attributed to asymmetric or symmetric ν(NCO) vibrations. Its ^1H n.m.r. spectrum in $CDCl_3$ (Figure 1.4) showed the usual resonances attributed to the η-p-cymene ring and in addition two doublets, at δ6.32 and 8.51 ppm, due to the olefinic protons of the isothiazoline ligand. Integration of the signals showed that the η -p-cymene ring and the isothiazoline ligand were present in a 1:1 molar ratio. A broad peak at ca. 3.5 ppm was attributed to the hydroxyl proton of the ligand in the canonical form (21c). On this evidence the product is formulated as $Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)\text{-}Cl_2(\eta^1\text{-}NC.OH.C_2H_2S)$ (22) in which the isothiazoline ligand has coordinated through the nitrogen atom, i.e. corresponding

Figure 1.4 The ^{1}H n.m.r. spectrum of $Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(\eta^1\text{-}NCOH.C_2H_2S)$ in $CDCl_3$ at 298 K.



to reaction of the ligand in the enol type canonical form (21c).



(22)

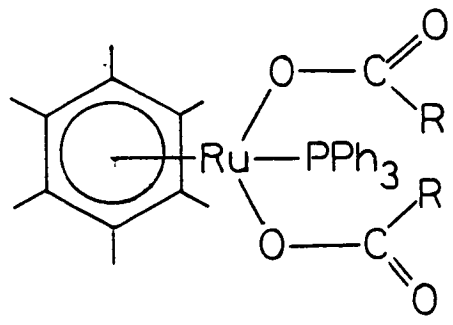
The η-benzene complex was prepared and characterised similarly.

1.3 Some Reactions of the Mononuclear Ruthenium(II) Carboxylates

A large variety of complexes can be prepared from the ruthenium(II) carboxylates discussed in the previous section. In general the carboxylate groups are easily displaced by a wide variety of ligands.

The reaction of $Ru(\eta\text{-}C_6Me_6)(O_2CR)_2.H_2O$ (R = Me, CF_3) with triphenylphosphine gives the yellow 1:1 adducts. The infrared spectrum of the bis(acetato) adduct shows medium intensity bands at 1640 and 1610 cm^{-1} assigned to $\nu_{asym}(OCO)$ and a strong band at 1360 cm^{-1} due to $\nu_{sym}(OCO)$, the value of $\Delta\nu$(250-280 cm^{-1}) being consistent with the presence of unidentate carboxylate groups. The complex is thus assigned the structure (23). All attempts to isolate the corresponding chloro-carboxylato-phosphine complexes $Ru(\eta\text{-}C_6Me_6)Cl(\eta^1\text{-}O_2CR)(PPh_3)$ from $Ru(\eta\text{-}C_6Me_6)Cl(\eta^2\text{-}O_2CR)$ and PPh_3 gave only small amounts

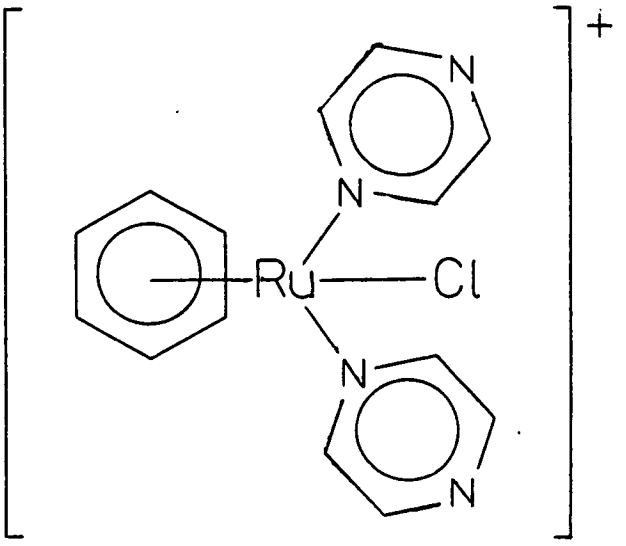
of the expected product together with a little $Ru(\eta\text{-}C_6Me_6)Cl_2(PPh_3)$, probably arising from rapid disproportionation of the mixed species.



(23)

The trifluoroacetate ligand of the complex $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ (24) is completely displaced by a wide variety of ligands. Thus, dissolving complex (24) in neat pyridine and subsequent treatment with $NH_4[PF_6]$ gives the known complex $[Ru(\eta\text{-}C_6H_6)Cl\ py_2][PF_6]$. Similarly the reaction with neat diphenylethylphosphine results in the formation of the $[Ru(\eta\text{-}C_6H_6)Cl(PEtPh_2)_2]^+$ cation. Treatment of (24) with 2,2'-bipyridyl in methanol gives a yellow solution and the solid obtained upon addition of $NH_4[PF_6]$ was identified as $[Ru(\eta\text{-}C_6H_6)Cl$-(2,2'-bipy)$][PF_6]$ by comparison with a genuine sample of this complex prepared from $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ and 2,2'-bipyridyl. Because complex (24) proved to be a useful precursor for synthesis of cationic species, of the type $[Ru(\eta\text{-}C_6H_6)Cl\ L_2]^+$, it was decided to investigate the reactions of the complex with potential binucleacting ligands, L-L (L-L = pyrazine, m-dithiane, 4,4'-bipyridyl). It was hoped to form a series of new complexes $[Ru(\eta\text{-}C_6H_6)Cl(L{-}{-}L)_2]X$, which might then couple to other metal centres, via the neutral ligand.

The infrared spectra of the pyrazine complexes $[Ru(\eta\text{-}C_6H_6)Cl(pyz)_2]X$ (X = PF_6, BPh_4) lack any bands due to bound $[CF_3CO_2]^-$ but do show bands at 845 and 610 cm^{-1} characteristic of η-benzene and bands at 1582, 1418, 1151, 1120 and 1054 cm^{-1} arising from vibrations associated with the pyrazine rings. A band at 300 cm^{-1} is clearly due to ν(Ru-Cl)(terminal) and a broad adsorption at 398 cm^{-1} was assigned tentatively to ν(Ru-N). Conductivity measurements in nitromethane have shown that the salts are 1:1 electrolytes. The ^1H n.m.r. spectrum of the hexafluorophosphate salt in CD_3NO_2 shows a singlet at 6.10 ppm due to the η-benzene and a complex multiplet at 8.72 ppm due to the pyrazine ligands, in the intensity ratio 6:8, and thus the cation is assigned the structure (25).



(25)

The m-dithiane and 4,4'-bipyridyl complexes have been characterised similarly. The complexes [Ru(η-arene)-Cl(L——L)][PF_6] (L——L = 2,2'-bipyridyl; 1,10-phenanthroline) have been shown to react further with dimethylphenyl-phosphine to give dicationic species [Ru(η-arene)(PMe_2Ph)-(L——L)][PF_6]$_2$. If however the complexes [Ru(η-C_6H_6)-Cl(L——L)$_2$]X (L——L = pyrazine; 4,4'-bipyridyl; m-dithiane) are reacted under similar conditions then the only product isolated was [Ru(η-C_6H_6)Cl(PMe_2Ph)$_2$]X, which has already been reported[13].

The reaction of [Ru(η-C_6H_6)Cl(m-dithiane)$_2$][PF_6] with a variety of metal complexes such as $PtCl_2$(1,5-cyclo-octadiene), $PtCl_2(PEt_3)_2$ and Rh(η^5-C_5Me_5)Cl(S_2PMe_2), gives a series of new species. However ^{1}H n.m.r. studies have shown that the solids isolated contained a mixture of products. When the reactions were carried out using [Ru(η-C_6H_6)Cl(pyz)$_2$][PF_6] in place of the m-dithiane complex then the solid recovered was largely unreacted starting material. A possible explanation of the latter observation may be that the free nitrogen atoms are not orientated so as to facilitate coordination to one metal centre.

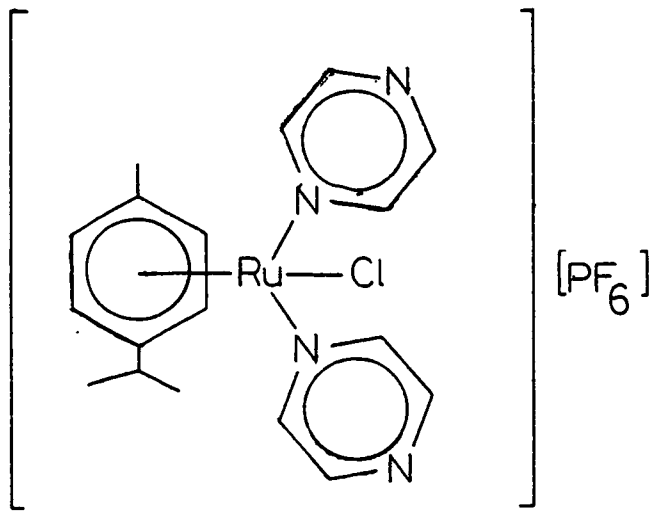
The carboxylates have also been found to be useful synthetic precursors for a variety of binuclear complexes. For example stirring Ru(η-C_6H_6)Cl(O_2CCF_3) in methanol in the presence of sodium tetraphenylboronate results in

the formation of an orange solid, the infrared spectrum of which contains no ν(OCO) band. The ^{1}H n.m.r. in CD_3NO_2 contains four η-benzene resonances at δ5.91, 5.75, 5.59 and 5.42 ppm, and three signals due to the η-methoxo group at δ4.55, 4.48 and 4.44 ppm. The signal in the ^{1}H n.m.r. spectrum at 5.92 ppm can be attributed to the cation $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ while the resonances at δ5.42 and 4.44 ppm can be attributed to the cation $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$, and the other resonances may be due to the mixed bridged cations $[Ru_2(\eta\text{-}C_6H_6)_2Cl_2(OMe)]^+$ and $[Ru(\eta\text{-}C_6H_6)Cl(OMe)_2]^+$. The triple bridged complex $[Ru_2(\eta\text{-}C_6Me_6)_2(O_2CCH_3)_3][PF$ has been reported[60] to be formed by reaction of $Ru(\eta\text{-}C_6Me_6)(O_2CCH_3)_2.H_2O$ with aqueous $K[PF_6]$. The reaction of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ or $Ru(\eta\text{-}C_6H_6)(O_2CMe)_2$ with aqueous sodium hydroxide or sodium carbonate leads to extensive decomposition. However, if either of these compounds are treated with sodium methoxide in methanol then a pale yellow solution results. Treatment of this solution with $Na[BPh_4]$ gives a microcrystalline yellow solid. Its ^{1}H n.m.r. spectrum in CD_3NO_2 shows the usual resonances due to the $[BPh_4]^-$ anion and two singlets at δ5.48 and 4.42 ppm which are attributed to the η-benzene and methoxy groups respectively. Integration of these signals is in the ratio 20:12:9 and thus the product was identified as the known tri-μ-alkoxo bridged complex $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$[68]. Reaction with sodium

ethoxide results in the formation of the analogous tri-μ-ethoxo salts. The carboxylates have also been shown to readily form μ-hydrido complexes on heating with propan-2-ol, probably via thermally unstable propan-2-oxides[30].

1.4.1 The reactions of $[M(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (M = Ru, Os) with potential binucleating ligands

Analogous complexes to these described above, containing the p-cymene ring, have been prepared by direct reaction of $[M(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (M = Ru, Os) with an excess of various ligands in methanol and subsequent treatment with $NH_4[PF_6]$ or $Na[BPh_4]$. For example the reaction of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ with pyrazine in methanol produces a red-brown solution and subsequent treatment of this solution with $NH_4[PF_6]$ leads to the slow deposition of brown needle crystals. The infrared spectrum of this product contains a terminal ν(Ru-Cl) band at 296 cm^{-1} and bands due to the pyrazine ligands at 1580, 1418, 1149, 1120 and 1052 cm^{-1} as well as bands attributable to a $[PF_6]^-$ anion. The ^1H n.m.r. spectrum of this product in CD_3NO_2 contains the usual resonances due to the p-cymene ring, and a complex multiplet at 8.82 ppm due to the pyrazine ligands. Integration of the signals indicated a ratio of one p-cymene ring to two pyrazine rings. This spectroscopic data together with conductivity measurements and microanalysis figures suggest that $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$ (26) is formed.



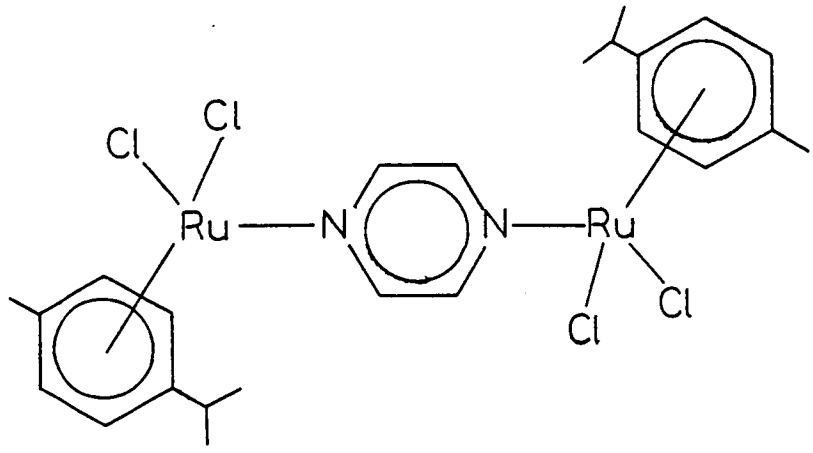
(26)

The products isolated from the reactions with m-dithiane and 4,4'-bipyridyl were characterised similarly. However the ^{1}H n.m.r. signals of these ligands in the benzene and p-cymene complexes were very broad and several of these compounds have therefore been better characterised by their $^{13}C\{^{1}H\}$ n.m.r. spectra (Table 1.6).

Unfortunately attempts to prepare mixed metal complexes by attachment to the uncoordinated nitrogen atoms of (26) were unsuccessful. The single crystal X-ray structure of this compound (Section 1.4.2) shows that the free nitrogen atoms are too for apart for effective bidentate coordination to one metal atom.

Interestingly, direct reaction of pyrazine with $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ in dry THF gives a brown, microcrystalline solid of empirical formula $\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2pyz$ (27), which was non-conducting in nitromethane. The ^{1}H n.m.r. spectrum in CD_3NO_2 shows a sharp resonance at δ9.10 ppm due to the pyrazine protons in addition to the usual arene signals, and integration confirms the stoichiometry indicated by the micro-analytical data. The infrared spectrum

contains a broad band due to ν(Ru-Cl)(terminal) at 290 cm^{-1}. The most reasonable structure is one in which pyrazine bridges two "Ru(η-arene)Cl_2" moieties in a manner well established in other areas of ruthenium chemistry[69].



(27)

1.4.2 The X-ray crystal structure of [Ru(η 1,4-$MeC_6H_4CHMe_2$)Cl($C_4H_4N_2$)$_2$][PF_6]

The crystal structure determination was carried out by V.K. Shah and L. Sawyer at Napier College, Edinburgh.

Details of the solution of the structure are given in the experimental section. The final atomic parameters are given in Table 1.7 and selected bond angles and distances in Table 1.8. The molecular structure of the cation is shown in Figure 1.5, a stereodiagram of the molecular structure of (26) in Figure 1.6, and a crystal packing diagram in Figure 1.7.

Figure 1.5 The structure of the cation $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_6H_4N_2)_2]^+$

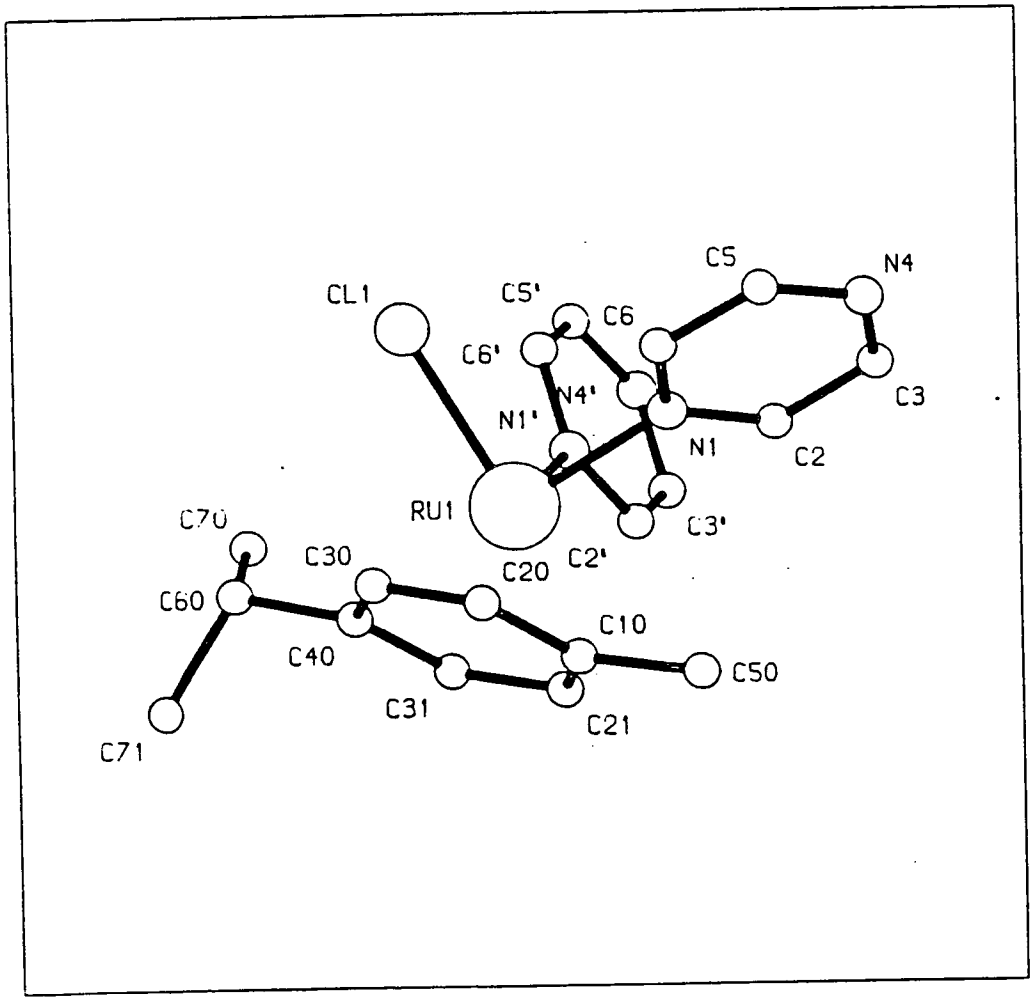
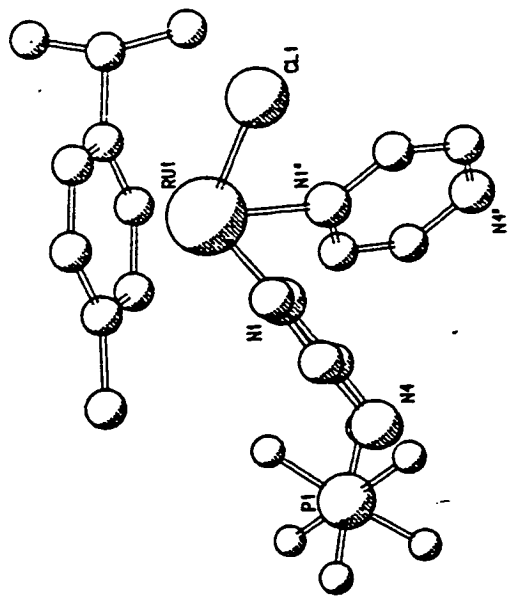


Figure 1.6 Stereodiagram of the molecular structure of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_6N_2)_2][PF_6]$



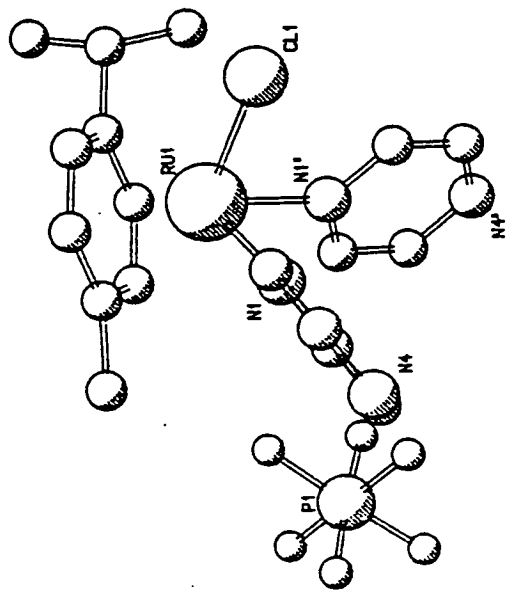
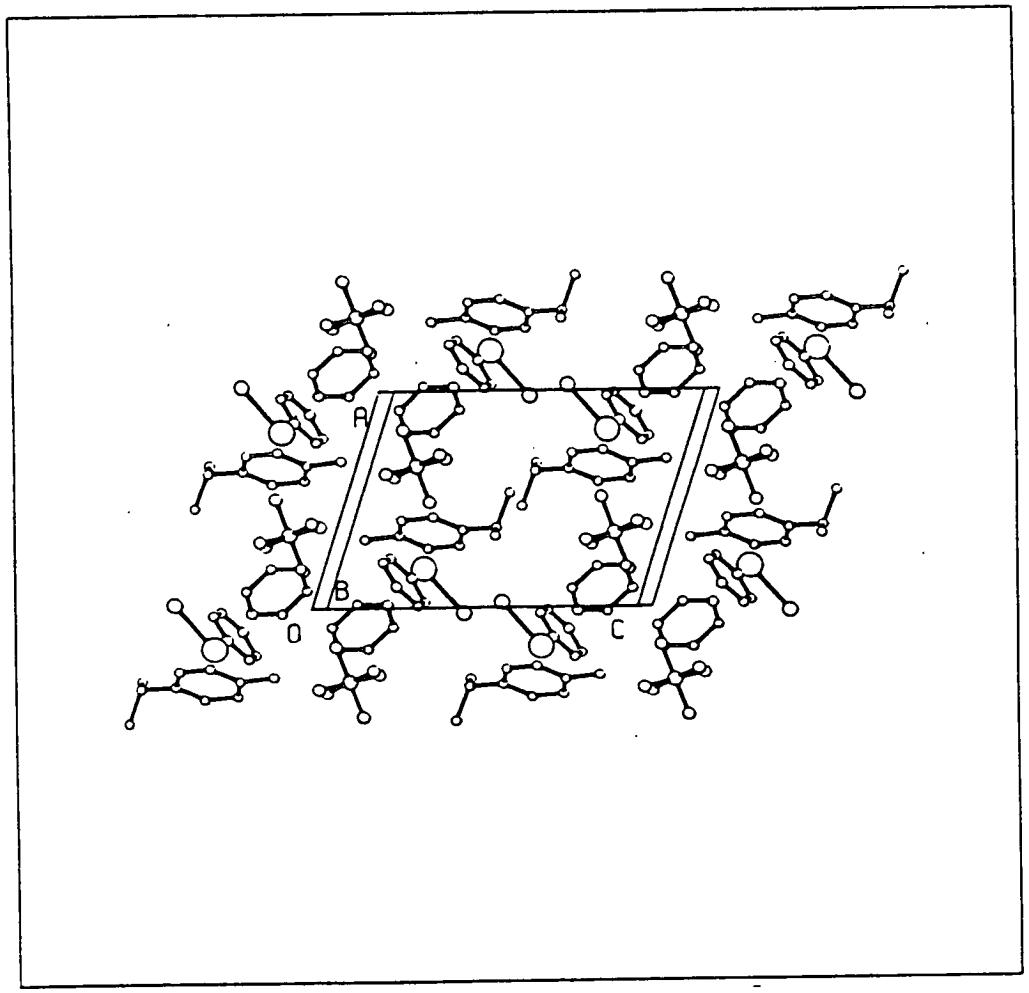


Figure 1.7 A crystal packing diagram for $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_4N_2)_2][PF_6]$



The coordination about the ruthenium atom is octahedral with the η-p-cymene ring and the other three ligands adopting a "piano-stool" configuration. The complex has similar geometry to that of $Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(PMe_2Ph)$ [45] with the Ru-C distances to the p-cymene not significantly different. There is also good agreement with the Ru-Cl distance. However, the p-cymene ring here shows no significant deviation from planarity. The rms deviation of the six atoms in the plane was 0.006 Å with no atom being more than 0.008 Å. The metal to ring centroid distance was 1.68 Å which is slightly greater than that found in the complexes $[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ [6] and $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4].MeOH$ [70] but is in agreement with the Ru-arene distance found by Bennett et al [45]. The methyl and iso-propyl substituents were bent towards the Ru by 3.0° and 1.2° respectively and thus the distortion is similar to that found for the Os complex. Also the atoms C71 and C70 are displaced by similar amounts (1.40 Å away and 0.99 Å towards the Ru) to those observed in both Ru and Os complexes.

The pyrazine ligands are both planar, the rms deviation being 0.009 Å and 0.007 Å for the N1 and N1' rings respectively. The Ru atom is 0.13 Å and 0.12 Å out of the ring planes and the distances, Ru-N, of 2.15 Å and 2.18 Å are slightly longer than those reported for the octahedral complexes of Ru(II) and Ru(III) by Gess et al [71].

The angles between the normals to the pyrazine ring planes was 87°. The distortion of the N1 ring, and, to a lesser extent the N1' ring is a consequence of their closeness to the $[PF_6]^-$ anion. The explanation for the inability of the complex to bind further metals through the distal ring nitrogens can be seen immediately from Figure 1.5. The separation is 6.89 Å which is much too great when compared with the 2.91 Å between the two bound N1, N1' atoms.

Finally, the $[PF_6]^-$ anion is octahedrally coordinated and does not appear to be distorted although the temperature factors for F1-F6 are higher than those for the rest of the non-hydrogen atoms.

1.5 Experimental

Microanalyses were by B.M.A.C. and the University of Edinburgh, Chemistry Department. Molecular weights were determined on a Perkin-Elmer Hitachi Model 115 osmometer calibrated with benzil. Infrared spectra were recorded in the 4000-200 cm^{-1} region on a Perkin Elmer 447 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates and potasium bromide discs, and in the region 400-33 cm^{-1} on a Hitachi F1S 3 spectrometer on polythene discs. Hydrogen-1-n.m.r. spectra were recorded on Varian Associates HA-100 and EM-360 spectrometers. Carbon-13 n.m.r. spectra were recorded on Varian CFT20, XL100 and Brucker WH360 spectrometers.

Fluorine-19 spectra were recorded on a Varian XL100 spectrometer operating in Fourier-transform mode at 94.1 MHz (^{19}F chemical shifts quoted in ppm to high frequency of $CFCl_3$). Phosphorous-31 n.m.r. spectra were recorded on a Jeol FX60 spectrometer operating at 24.2 MHz (^{31}P n.m.r. chemical shifts quoted in ppm to high frequency of 85% H_3PO_4). Conductivity measurements were obtained on a Portland Electronics 310 conductivity bridge at 298 K. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Ruthenium trichloride trihydrate and sodium hexachloroosmate(IV) were supplied by Johnson Matthey, P.L.C., isothiazadine was supplied by Dr. I.A. Gosney, of Edinburgh University and all other starting materials were obtained from normal commercial suppliers.

The complexes $[Ru(\eta\text{-arene})Cl_2]_2$ (η-arene = C_6H_6, $1,4\text{-}MeC_6H_4CHMe_2$ or $1,3,5\text{-}C_6H_3Me_3$) were prepared by reaction of ethanolic hydrated $RuCl_3$ (which had first been activated by repeated evaporation of its aqueous solution on an oil bath[9]) with the appropriate cyclohexadiene[3,5]. The hexamethylbenzene and durene complexes $[Ru(\eta\text{-arene})X_2]_2$ (arene = C_6Me_6, $1,2,4,5\text{-}C_6H_2Me_4$) were obtained by heating the p-cymene complex with a large excess of molten arene at *ca.* 160-180°C [72]. $[Ru(\eta\text{-}C_6H_6)X_2]_2$ (X = Br, I) were prepared by the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with the

appropriate lithium halide in water[4,45]. $[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ was prepared by the reaction of α-phellandrene with ethanolic $Na_2[OsCl_6]$[9]. The complex $Ru(\eta\text{-}C_6H_6)Cl(acac)$ was made by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with thallium(I)acetylacetonate[7]. All reactions were carried out under dry nitrogen using degassed solvents, although the isolated complexes were air stable. Analytical data for the new complexes are given in Table 1.1, infrared data for the arene ruthenium(II) carboxylates are in Tables 1.2 and 1.4, ^1H n.m.r. data for these compounds are in Tables 1.3 and 1.5 and $^{13}C\text{-}\{^1H\}$ n.m.r. data in Table 1.6.

Crystal Structure Determination of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_4N_2)_2][PF_6]$

Crystals suitable for X-ray analysis were obtained by cooling a methanolic solution of the complex to 273 K for 48 hours. A brown, elongated crystal (0.2 x 0.4 x 0.6 mm) was chosen and precession photographs indicated a triclinic space group. Accurate cell dimensions were obtained by least squares refinement of 18 reflections on a Nonius CAD4 diffractometer with monochromated Mo-K_α radiation.

Crystal Data: $RuClPF_6(N_4C_{18}H_{22})$ M = 573.83; a = 9.265(2), b = 9.684(4), c = 12.969(2) Å, α = 86.51(2)°, β = 72.89(2)°, γ = 85.59(2)°, V = 1107.9 Å^3. D_c = 1.73 g cm^{-3}, D_m = 1.72 g cm^{-3} (by flotation), Z = 2, F(000) = 576, $\mu(M_o-k_\alpha)$ = 9.54 cm^{-1}, $\lambda(M_o - k_\alpha)$ = 0.71069 Å. There is one molecule in the asymmetric unit assuming space group $P\bar{1}$.

Intensity data were collected by an $\omega = 2\theta$ scan of $1.5(0.8 + 0.35\tan\theta)$ for varying times up to a maximum of 60 s such that where possible $I > 3\sigma(I)$. A standard reflection was monitored regularly throughout data collection but no decay was observed. After corrections for L_p effects, 2030 out of 3866 reflections measured to $\theta_{max} = 25^\circ$ had $I > 3\sigma(I)$. No absorption correction was applied.

Structure Solution and Refinement

The structure was solved by the conventional Patterson and difference Fourier techniques. A Patterson map revealed the Ru-Ru vector and the remaining atoms were obtained from difference Fourier syntheses. Refinement of the structure by least squares reduced the R factor from 0.295 to 0.063 in 3 cycles with Ru, Cl and P atoms refined anisotropically. The hydrogen atoms were placed in their predicted positions and allowed to ride on the atoms to which they were attached, for a further cycle of least squares.

A weighting scheme of the form $W = 0.818/(\sigma^2(F) + 0.001\ F^2)$ was applied for a final cycle and gave R = 0.059 (Rw = 0.070). The maximum shift/esd at this stage was 0.014 and no significant residual electron density was observed in the final difference Fourier map. No extinction correction was applied but two reflections (2 3 2) and (-2 4 2) were omitted because of likely extinction. The atomic scattering factor for Ru was taken from reference 73.

Figure 1.5 shows the geometry of the cation together with the atomic designations. Figure 1.6 shows a general stereoview of the non-hydrogen atoms while Figure 1.7 shows the crystal packing. No short intermolecular contacts were observed. Table 1.7 gives the final fractional coordinates and selected bond distances and angles are presented in Table 1.8. The SHELX[74] program was used for the crystallographic calculations.

Acetato(chloro)(η-benzene)ruthenium(II), $Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$

(1) A suspension of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.16 g, 0.32 mmol) in acetic acid (10 ml) and acetic anhydride (2ml) was heated under reflux for periods of 6h to 5d (depending on the quality of the starting material) to give a dark red-brown solution. This was filtered hot to remove brown solid. On cooling the filtrate deposited the product as a dark red-brown crystalline solid (90 mg, 52%), m.p. 208°C (decomp.).

(2) A suspension of $Ru(\eta\text{-}C_6H_6)Cl(acac)$ (0.24 g, 0.93 mmol) in acetic acid (35 ml) and acetic anhydride (25 ml) was stirred at 75°C for 5d. Solvents were removed in vacuo and the residue triturated with ether to give the orange, micro-crystalline product (160 mg, 59%).

Acetato(chloro)(η-p-cymene)ruthenium(II), $Ru(\eta\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)$

A solution of $[Ru(\eta\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (0.16 g, 0.26 mmol) in acetic acid (20 ml) and acetic anhydride (5 ml) was heated under reflux for 3h. The mixture was evaporated to ca. half-volume, ether and n-heptane were added, and the solution was set aside at 0°C for 24h. The red-brown crystalline solid was filtered, washed with a few ml of ether and air-dried. Yield 180 mg (56%), m.p. 172-173°C.

(η-Benzene)(chloro)(trifluoroacetato)ruthenium(II), $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$

$[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.20 g, 0.40 mmol) was added to a mixture of trifluoroacetic acid (15 ml) and trifluoroacetic anhydride (1 ml) and refluxed for 2½h. The solution was then filtered hot to remove any undissolved starting material. The orange filtrate was evaporated under reduced pressure to ca. half volume and the product precipitated as an orange powder by addition of ether. After filtration, washing with ether and air-drying the yield was 150 mg (55%), m.p. 232-235°C (decomp.).

The corresponding bromo- and iodo-complexes $Ru(\eta\text{-}C_6H_6)X(O_2CCF_3)$ (X = Br, I) were prepared similarly, although both were too insoluble for their n.m.r. spectra to be recorded and the latter was not analytically pure.

Acetato(chloro)(η-hexamethylbenzene)ruthenium(II), $Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$

(1) A mixture of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.20 g, 0.3 mmol) and anhydrous sodium acetate (0.30 g, 3.66 mmol) was stirred in acetone (50 ml) at room temperature for 22h. After centrifuging the supernatant liquid was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane/n-hexane to give the product as bright orange microcrystals (120 mg, 56%).

(2) A mixture of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.20 g, 0.3 mmol) and silver acetate (0.10 g, 0.6 mmol) in benzene (25 ml) was stirred at room temperature for 2.5h. Work-up as under (1) gave the product (120 mg, 56%), m.p. 209-212°C (decomp.).

Acetato(bromo)(η-durene)ruthenium(II), $Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Br(O_2CMe)$

A mixture of $[Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Br_2]_2$ (0.39 g, 0.5 mmol) and silver acetate (0.17 g, 1.0 mmol) was stirred in benzene (60 ml) at room temperature for 5h. Centrifugation gave a red-violet solution. Solvent was

removed under reduced pressure and the residue was recrystallized from dichloromethane/n-hexane to give orange-red crystals of the product (240 mg, 63%).

Chloro(η-hexamethylbenzene)(trifluoroacetato)-ruthenium(II), $Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$

A mixture of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.20 g, 0.3 mmol) and silver trifluoroacetate (0.13 g, 0.6 mmol) in benzene (45 ml) was stirred for 6h at room temperature. The orange-red solution obtained after removal of AgCl was evaporated to dryness under reduced pressure and the residue was recrystallized from dichloromethane/n-hexane to give bright orange microcrystals (123 mg, 50%).

Reaction of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ with trifluoroacetic acid

$[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.10 g, 0.3 mmol) was added to trifluoroacetic acid (3 ml) and the mixture stirred at 75°C for 5h to give a dark red solution. The acid was removed in vacuo leaving a yellow-brown oil which gave an orange solid on addition of ether. Recrystallization from dichloromethane/n-hexane gave pale yellow, microcrystalline $Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)CF_3CO_2H$ (122 mg, 45% yield).

The same product was obtained from $Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$ (0.09 g, 0.25 mmol) and trifluoroacetic acid (2 ml) at 46°C for 10 min. Yield: 98 mg (74%).

Bis(acetato)(η-hexamethylbenzene)ruthenium(II) monohydrate, $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$

A mixture of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.40g, 0.6 mmol) and silver acetate (0.30 g, 2.6 mmol) in benzene (30 ml) was stirred at room temperature for 12h. The solution was either centrifuged or filtered through Celite to remove AgCl and was evaporated to dryness under reduced pressure. The residue was recrystallized from ether/n-hexane and dried in vacuo to give yellow needles of the product (365 mg, 80%), m.p. 162-165°C (decomp.).

The other arene ruthenium bis(acetates) were prepared similarly and were recrystallized from dichloromethane/n-hexane. The durene complex tenaciously retains dichloromethane and was therefore recrystallised from ether/n-hexane.

(η-Hexamethylbenzene)bis(trifluoroacetato)ruthenium(II) monohydrate, $Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2.H_2O$

A mixture of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ (0.10 g, 0.25 mmol) and trifluoroacetic acid (2 ml) was stirred at 45°C for 20 min. to give a deep red solution. The

acid was removed in vacuo to give a wine-red oil which dissolved in ether (15 ml) to form a pale yellow solution. The volume was reduced to ca. 3 ml and the solution was cooled to 0°C affording fine yellow crystals of the product (80 mg, 63%).

The other arene ruthenium bis(trifluoroacetates) were obtained similarly, although the method given below could also be used.

(η-Benzene)bis(trifluoroacetato)ruthenium(II) monohydrate, $Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$

$[Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$ (0.20 g, 0.4 mmol) was treated with silver trifluoroacetate (0.35 g, 1.58 mmol) for 6h at room temperature. The usual work-up gave the product as an orange-yellow powder (150 mg, 44%), m.p. 128-130°C.

Reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with Benzoic acid

$[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.20 g, 0.40 mmol) was shaken in methanol (15 ml) containing benzoic acid (1 g) for 24 h. Addition of $Na[BPh_4]$ (0.4 g) gave an orange solid. After filtration, washing with methanol, and drying in vacuo the yield of product, m.p. 205°C (decomp.) was 160 mg (50%). It was identified as $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$ by comparison of its ^1H n.m.r. spectrum with that of an authentic sample.

Isothiazolinato(dichloro)(η-benzene)ruthenium(II), $Ru(\eta\text{-}C_6H_6)Cl_2(NCOH.C_2H_2S)$

$[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g, 0.20 mmol) was shaken in methanol (10 ml) containing isothiazoline (0.1 g) for 16 hours. The red solid formed was filtered off, washed with methanol and dried in vacuo (55 mg, 20%) m.p. 220°C (decomp.).

Isothiazolinato(dichloro)(η-p-cymene)ruthenium(II), $Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2(NCOH.C_2H_2S)$

$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (0.15 g, 0.25 mmol) was shaken in methanol (15 ml) containing isothiazoline (0.1 g) for 24 hours. The solution was then evaporated to ca. half volume and diethylether added. The orange microcrystalline solid was filtered, washed with a little diethyl ether and air dried. Yield (140 mg, 70%), m.p. 161-163°C.

Reactions of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ with ligands

1. Pyridine

A solution of the complex (0.15 g, 0.45 mmol) in pyridine (5 ml) was stirred for 1 hour at room temperature. Pyridine was evaporated in vacuo and the resulting dark oil was dissolved in methanol to give a yellow solution. This was filtered and added to a solution containing $NH_4[PF_6]$ (0.3 g) in methanol (8 ml). The yellow solid

product which precipitated was filtered in air, washed with ether and methanol, and dried in vacuo at 54°C (180 mg, 76%), m.p. 227°C. The spectroscopic properties were identical with those previously reported for $[Ru(\eta\text{-}C_6H_6)Cl(py)_2][PF_6]$ [6,16].

2. Ethyldiphenylphosphine

The complex (0.1 g, 0.3 mmol) was stirred in the neat ligand (1.5 ml) for 4 hours to give a red solution. Excess of ligand was pumped off and the residue redissolved in methanol to which $Na[BPh_4]$ (0.4 g) was added. After several minutes a bright yellow precipitate of $[Ru(\eta\text{-}C_6H_6)Cl(PEtPh_2)_2][BPh_4]$ formed. This was filtered off, washed with ether and methanol and dried in vacuo (270 mg, 91%), m.p. 186-188°C (decomp.).

3. 2,2'-Bipyridyl

A suspension of the complex (0.15 g, 0.45 mmol) in degassed methanol (30 ml) containing an excess of 2,2'-bipyridyl was refluxed for 3 hours. The solid which precipitated on addition of $NH_4[PF_6]$ (0.3 g) was filtered off, washed with methanol and dried in vacuo (140 mg, 59%), m.p. 275°C (decomp.). The spectroscopic properties were identical with those previously reported for $[Ru(\eta\text{-}C_6H_6)Cl(2,2'\text{-bipy})][PF_6]$ [17].

4. Alkoxides

A suspension of Na_2CO_3 (0.3 g) in methanol (15 ml) was treated with the complex (0.1 g, 0.3 mmol) and stirred for 1 hour to give a yellow solution. This was filtered and $Na[BPh_4]$ (0.3 g) was added to give a yellow precipitate. After filtration, washing with methanol, drying in vacuo, the yield of product, m.p. 198°C (decomp.) was 70 mg (30%). It was identified as $[Ru_2(\eta C_6H_6)_2(OMe)_3][BPh_4]$ by comparison of its ^1H n.m.r. spectrum with that of an authentic sample[14].

The same complex was obtained in 65% yield from the reaction of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ (0.1 g) with a solution of sodium methoxide prepared from sodium (0.3 g) and methanol (15 ml). Likewise, reaction of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ with ethanolic sodium ethoxide gave $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][PF_6]$, m.p. 191°C (decomp.) (45%)[14].

5. Pyrazine

A suspension of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ (0.15 g, 0.45 mmol) in degassed methanol (20 ml) was treated with an excess of pyrazine (0.5 g) and the mixture was shaken for 2 hours. Addition of $Na[BPh_4]$ (0.35 g) to the orange solution gave $[Ru(\eta\text{-}C_6H_6)Cl(pyz)_2][BPh_4]$, m.p. 185-187°C as a microcrystalline, golden-yellow solid which was filtered off, washed with methanol and ether, and dried in vacuo (260 mg, 82%). The corresponding $[PF_6]^-$ salt was obtained similarly using $NH_4[PF_6]$ in place of $Na[BPh_4]$.

6. 4,4'-Bipyridyl

A suspension of $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ (0.12 g, 0.36 mmol) in methanol (20 ml) was shaken with an excess of 4,4'-bipyridyl for 2d to give a red solution. Addition of $Na[BPh_4]$ (0.2 g) gave a yellow-brown solid $[Ru(\eta\text{-}C_6H_6)Cl(4,4'\text{-bipy})_2][BPh_4]$, m.p. 173-174°C (decomp.), which was filtered off, washed with methanol, and air-dried. Yield: 220 mg (71%).

7. m-Dithiane

A reaction carried out as above, using 1,3-dithiane and $NH_4[PF_6]$, gave $[Ru(\eta\text{-}C_6H_6)Cl(\underline{m}\text{-dithiane})_2]PF_6$, m.p. 210-212°C, in 67% yield.

Reactions of $Ru(\eta\text{-}C_6Me_6)(O_2CR)_2$ with ligands

1. Alkoxides

To a solution of sodium methoxide freshly prepared from sodium (0.4 g) and methanol (10 ml) was added $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ (0.1 g, 0.25 mmol).

The mixture was stirred for 1.5h to give a yellow solution. This was filtered and treated with $Na[BPh_4]$ (0.3 g) to give a yellow precipitate. After filtration, washing with methanol, and drying in air this was identified as $[Ru_2(\eta\text{-}C_6Me_6)_2(OMe)_3][BPh_4]$, m.p. 169-173°C (decomp.). (90 mg, 38%) by ^1H n.m.r. spectroscopy[14].

2. Triphenylphosphine

A mixture of $Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2.H_2O$ (0.10 g, 0.20 mmol) and triphenylphosphine (0.06 g, 0.22 mmol) in benzene (25 ml) was stirred at room temperature for 3.5h. Solvent was evaporated under reduced pressure and the product $Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PPh_3)$ was precipitated by addition of n-hexane (30 ml). After washing with two 30 ml portions of n-hexane and drying in vacuo, the yield of orange-yellow crystals was 90 mg (61%).

The corresponding bis(acetate) was prepared similarly from $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$.

Complexes formed from potentially binucleating ligands with $[M(\eta\text{-arene})Cl_2]_2$ (M = Ru, arene = 1,4-$MeC_6H_4CHMe_2$, C_6Me_6; M = Os, arene = 1,4-$MeC_6H_4CHMe_2$)

1. $[Ru(\eta\text{-}C_6Me_6)Cl(m\text{-dithiane})_2][BPh_4]$

A suspension of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.12 g, 0.18 mmol) in methanol containing an excess of m-dithiane (0.23 g) was shaken for 4h to give a yellow solution. After filtration to remove unreacted starting material, addition to methanolic $Na[BPh_4]$ gave the product as a bright yellow precipitate. This was filtered off, washed with water, methanol and ether, and dried in vacuo at 54°C.
Yield: 130 mg (42%), m.p. 108°C.

2. [Os(η-p-cymene)Cl(pyz)$_2$][PF$_6$]

[Os(η-p-cymene)Cl$_2$]$_2$ (0.1 g, 0.13 mmol) was shaken in methanol (20 ml) containing an excess of pyrazine (0.3 g) for 3h. The resulting solution was filtered directly into a methanolic solution of $NH_4[PF_6]$. After 3d at 0°C the yellow-brown solid product which had deposited was filtered off and air-dried. Yield: 160 mg, (67%), m.p. 178-184°C.

Similarly prepared in 68% yield from [Os(η-p-cymene)-Cl$_2$]$_2$ and m-dithiane in methanol was [Os(η-p-cymene)-Cl(m-dithiane)$_2$][BPh$_4$], m.p. 168-170°C and in 77% yield from [Ru(η-p-cymene)Cl$_2$]$_2$ and pyrazine in methanol yellow-brown needles of [Ru(η-p-cymene)Cl(pyz)$_2$][PF$_6$], m.p. 185-188°C.

3. [Ru(η-p-cymene)Cl(4,4'-bipy)$_2$][BPh$_4$]

[Ru(η-p-cymene)Cl$_2$]$_2$ (0.2 g, 0.16 mmol) was shaken with a solution of 4,4'-bipyridyl (0.3 g) in methanol (25 ml) for 9 h. The mixture was filtered and $Na[BPh_4]$ was added. The creamy-brown precipitate was filtered off, washed with methanol, and dried in vacuo. Yield: 290 mg (95%), m.p. 122-125°C (decomp.).

4. {Ru(η-p-cymene)Cl$_2$}$_2$(μ-pyz)

To a solution of [Ru(η-p-cymene)Cl$_2$]$_2$ (0.2 g, 0.16 mmol) in dry THF (25 ml) was added pyrazine (0.03 g,0.38 mmol). The mixture was heated under reflux for 1 h and the brown microcrystalline solid which deposited was filtered off, washed with ether, and dried in vacuo. Yield: 140 mg, (66%), m.p. 232°C.

Table 1.1 Analytical data for arene ruthenium(II) carboxylates and related complexes of ruthenium and osmium[a]

	%C	%H	%Other
$Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$	35.4(35.1)	3.5(3.3)	13.3(13.0)(Cl)[b]
$Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$	29.5(29.3)	2.0(1.9)	10.8(10.8)(Cl)
$Ru(\eta\text{-}C_6H_6)Br(O_2CCF_3)$	25.2(25.8)	1.9(1.6)	
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)$	43.6(43.7)	5.2(5.2)	11.0(10.8)(Cl)[c]
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Br(O_2CMe)$	38.6(38.5)	4.4(4.55)	21.8(21.4)(Br)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CMe)$	41.5(41.8)	4.8(4.75)	11.4(11.25)(Cl)[d]
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Br(O_2CMe)$	36.6(36.7)	4.2(4.2)	22.1(22.2)(Br)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CCF_3)$	35.5(35.7)	3.4(3.25)	9.9(9.6)(Cl)
			15.2(15.4)(F)
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Cl(O_2CMe)$	43.8(43.7)	5.2(5.2)	10.7(10.8)(Cl)
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Br(O_2CMe)$	38.3(38.5)	4.6(4.55)	22.0(21.4)(Br)
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$	47.0(47.0)	6.0(5.9)	10.1(9.9)(Cl)[e]
$Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)$	41.9(41.8)	5.3(5.2)	20.05(19.9)(Br)
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$	40.8(40.8)	4.6(4.4)	7.6(8.6)(Cl)
			14.3(13.9)(F)

Table 1.1 (contd.)

	%C	%H	%Other
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3).CF_3CO_2H$	37.0(36.5)	3.7(3.6)	7.3(6.7)(Cl)[f]
			21.6(21.7)(F)
$Ru(\eta\text{-}C_6H_6)(O_2CMe)_2$	38.8(40.3)	4.2(4.0)	20.3(21.4)(O)
$Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$	28.4(28.4)	1.9(1.9)	26.8(26.95)(F)
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CMe)_2$	48.0(47.6)	5.8(5.7)	17.9(18.1)(O)[g]
			28.5(28.6)(Ru)
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CCF_3)_2.H_2O$	35.1(35.1)	3.4(3.3)	23.7(23.8)(F)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CMe)_2$	46.15(46.0)	5.4(5.3)	18.1(18.9)(O)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CCF_3)_2.H_2O$	33.7(33.55)	3.0(3.0)	23.7(24.5)(F)
			30.3(29.8)(Ru)
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)(O_2CMe)_2.H_2O$	45.4(45.3)	6.0(5.9)	21.7(21.6)(O)
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)(O_2CCF_3)_2.H_2O$	35.4(35.1)	3.5(3.3)	22.9(23.8)(F)
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$	48.1(48.1)	6.6(6.5)	20.0(20.05)(O)[h]
			25.0(25.3)(Ru)
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2.H_2O$	37.45(37.9)	4.0(3.9)	21.5(22.4)(F)

Table 1.1 (contd.)

	%C	%H	%Other
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PPh_3)$	63.5(63.45)	6.1(6.1)	5.1(4.8)(P)
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PPh_3)$	54.3(54.3)	4.5(4.4)	4.1(4.1)(P)
			14.8(15.2)(F)
$[Ru(\eta\text{-}C_6H_6)Cl(pyz)_2][BPh_4]$	64.4(65.7)	5.1(5.0)	7.7(8.0)(N)
			5.0(5.1)(Cl)
$[Ru(\eta\text{-}C_6H_6)Cl(pyz)_2][PF_6]$	32.6(32.4)	2.9(2.7)	10.5(10.8)(N)
$[Ru(\eta\text{-}C_6H_6)Cl(4,4'\text{-bipy})_2][BPh_4]$	69.8(70.4)	5.1(5.0)	6.3(6.6)(N)
			4.3(4.2)(Cl)
$[Ru(\eta\text{-}C_6H_6)Cl(\underline{m}\text{-dithiane})_2][PF_6]$	28.2(28.0)	3.8(3.7)	
$[Ru(\eta\text{-}C_6Me_6)Cl(\underline{m}\text{-dithiane})_2][BPh_4]$	60.3(61.5)	6.4(6.3)	
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$	32.5(32.5)	3.3(3.3)	8.1(8.4)(N)
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(\underline{m}\text{-dithiane})_2][BPh_4]$	53.9(54.9)	5.6(5.5)	
$\{Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\}_2(\mu\text{-pyz})$	40.6(41.6)	4.5(4.7)	4.1(4.1)(N)
			20.7(20.5)(Cl)
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$	37.4(37.5)	4.0(3.9)	9.6(9.7)(N)
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(4,4'\text{-bipy})_2][BPh_4]$	70.6(71.8)	5.6(5.6)	6.4(6.2)(N)

Table 1.1 (contd.)

	%C	%H	%Other
$Ru(\eta\text{-}C_6H_6)Cl_2(NCOH.C_2H_2S)$	31.6(30.8)	2.7(2.6)	3.7 (4.0)(N)
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2\text{-}(NCOH.C_2H_2S)$	38.2(38.3)	4.2(4.2)	3.3(3.4)(N)

a Calculated values in parenthesis

b Mol. wt. (acetone, 45°C) 283(274)

c Mol. wt. (acetone, 45°C) 345(330)

d Mol. wt. (CH_2Cl_2, 25°C) 341(315)

e Mol. wt. (CH_2Cl_2, 25°C) 360(357)

f Mol. wt. (CH_2Cl_2, 25°C) 1047(1051, dimer)

g Mol. wt. (CH_2Cl_2, 25°C) 371(353)

h Mol. wt. (CH_2Cl_2, 25°C) 407(399)

Table 1.2 Selected bands in the IR spectra of arene ruthenium(II) carboxylates[a,b]

Compound	ν_{sym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$
$Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$	1510(s,br)	1470(s),1410(s)	40-100
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)$	1512(s)	1465(vs),1382(s)	50-130
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Br(O_2CMe)$	1515(vs)	1470(vs),1450(ssh).1387(s)	45-130
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CMe)$	1510(vs)	1475(vs),1410(s),1387(vs)	35-130
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Br(O_2CMe)$	1525(msh),1505(s)	1475(vs),1412(s)	50-110
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Cl(O_2CMe)$	1515(vs)	1460(vs),1410(m),1385(m)	55-130
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Br(O_2CMe)$	1518(s)	1475(vs),380(m)	45-140
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$	1515(s)	1470(vs),1420(s),1385(s)	45-130
$Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)$	1510(s)	1465(vs),1410(vs),1380(s)	45-130
$Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$	1720(sh),1685(vs)	1418(m)	267
$Ru(\eta\text{-}C_6H_6)Br(O_2CCF_3)$	1720(sh),1685(vs)	1415(w)	270
$Ru(\eta\text{-}C_6H_6)I(O_2CCF_3)$	1720(sh),1690(br,vs)	1410(w)	280
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CCF_3)$	1712(vs),1685(vs), 1580(m),1530(s)	1440(m),1402(vs)	90-310
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$	1690(vs),1655(vs)	1450(mbr),1400(vs),1388(vs)	205-302
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)CF_3CO_2H$	1782(s),1720(m), 1648(vs)	1445(m),1385(m)	203-397

Table 1.2 (contd.)

Compound	ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$
$Ru(\eta\text{-}C_6H_6)(O_2CMe)_2$	1625(s),1565(s), 1538(s)	1475(vs),1435(vs)	60-100(bd)
		1370(vs),1315(vs)	310(ud)
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CMe)_2$	1630(vs),1585(m,sh) 1517(s)	1475(vs),1380(vs) 1362(vs),1310(vs)	40-155(bd) 310(ud)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CMe)_2$	1620(vs),1570(m), 1510(m)	1470(vs),1312(vs)	40-115(bd) 310(ud)
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)(O_2CMe)_2.H_2O$	1565(vs),1515(vs)	1470(vs),1445(vs),1340(vs)	45-100(bd) 225(ud)
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$	1565(s)	1470(sh),1410(sh),1395(vs) 1342(s)	95-223(ud)
$Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$	1675(vs),1580(w)	1440(s),1430(s)	140-245
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CCF_3)_2.H_2O$	1675(vs),1580(w)	1475(m),1430(s)	105-245
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CCF_3)_2.H_2O$	1670(vs),1530(w)	1442(s),1380(s)	88-290
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)\text{-}(O_2CCF_3)_2.H_2O$	1685(vs),1590(w,sh)	1445(vs),1432(vs),1382(s)	145-293
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2.H_2O$	1685(vs),1612(s), 1565(vs)	1438(s),1385(s)	127-300

Table 1.2 (contd.)

Compound	ν_{asym}(OCO)	ν_{sym}(OCO)	$\Delta\nu$
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PPh_3)$	1640(m),1610(m)	1360(s)	250-280(ud)
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PPh_3)$	1710(vs),1690(vs)	1390(m)	300-320(ud)

[a] Spectra run in Nujol and hexachlorobutadiene mulls

[b] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad; ud, unidentate; bd, bidentate

Table 1.3 ^{1}H n.m.r. data for arene ruthenium(II) carboxylates and derived complexes

Compound	Solvent	δ η-arene	δ acetate	δ other
$Ru(\eta\text{-}C_6H_6)Cl(O_2CMe)$	$CDCl_3$	5.76 (s, $C_6\underline{H}_6$)	1.87	
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(O_2CMe)$	$CDCl_3$	5.63, 5.44 (AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 6Hz), 2.94 (sp. $C\underline{H}Me_2$), 2.31 (s, Me), 1.37 (d, $CH\underline{Me}_2$, $\underline{J}$ 7Hz)	1.82	
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Br(O_2CMe)$	$CDCl_3$	5.41, 5.61 (AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 6Hz), 2.93 (m, $C\underline{H}Me_2$), 2.31 (s, Me), 1.39 (d, $CH\underline{Me}_2$, $\underline{J}$ 7Hz)	1.80	
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CMe)$	$CDCl_3$	5.0 (s, $C_6\underline{H}_3$), 2.25 (s, $C_6\underline{Me}_3$)	1.83	
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Br(O_2CMe)$	$CDCl_3$	5.0 (s, $C_6\underline{H}_3$), 2.27 (s, $C_6\underline{Me}_3$)	1.81	
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Cl(O_2CMe)$	$CDCl_3$	5.23 (s, $C_6\underline{H}_2$), 2.18 (s, $C_6\underline{Me}_4$)	1.83	
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)Br(O_2CMe)$	$CDCl_3$	5.29 (s, $C_6\underline{H}_2$), 2.20 (s, $C_6\underline{Me}_4$)	1.85	
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$	$CDCl_3$	2.17 (s, $C_6\underline{Me}_6$)	1.79	
$Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)$	$CDCl_3$	2.15 (s, $C_6\underline{Me}_6$)	1.77	
$Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$	CD_3NO_2	5.88 (s, $C_6\underline{H}_6$)		

Table 1.3 (contd.)

Compound	Solvent	δ η-arene	δ acetate	δ other
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$	$CDCl_3$	2.0(s,$C_6\underline{Me}_6$)		
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3).CF_3CO_2H$	$CDCl_3$	2.02(s,$C_6\underline{Me}_6$)		
$Ru(\eta\text{-}C_6H_6)(O_2CMe)_2$	$CDCl_3$	5.80(s,$C_6\underline{H}_6$)	1.92	
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CMe)_2$	$CDCl_3$	5.79,5.57(AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 6Hz),2.85(sp,$C\underline{H}Me_2$), 2.23(s,Me),1.33(d,$CH\underline{Me}_2$), $\underline{J}$ 7Hz)	1.90	
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CMe)_2$	$CDCl_3$	5.09(s,$C_6\underline{H}_3$),2.26(s,$C_6\underline{Me}_3$)	1.90	
$Ru(\eta\text{-}1,2,4,5\text{-}C_6H_2Me_4)(O_2CMe)_2.H_2O$	$CDCl_3$	5.39(s,$C_6\underline{H}_2$),2.14(s,$C_6\underline{Me}_4$)	1.93	4.3(H_2O)
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$	$CDCl_3$	2.13(s,$C_6\underline{Me}_6$)	1.95	
$Ru(\eta\text{-}C_6H_6)(O_2CCF_3)_2.H_2O$	d^6-DMSO	6.15(s,$C_6\underline{H}_6$)		5.91(H_2O)
	CD_3CN	5.68(s,$C_6\underline{H}_6$)		5.77(H_2O)
$Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(O_2CCF_3)_2.H_2O$	$CDCl_3$	5.63,5.44(AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 6Hz),2.90(sp,$C\underline{H}Me_2$), 2.21(s,Me),1.36(d,$CH\underline{Me}_2$, $\underline{J}$ 7Hz)		
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CCF_3)_2.H_2O$	$CDCl_3$	5.03(s,$C_6\underline{H}_3$),2.13(s,$C_6\underline{Me}_3$)		
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2.H_2O$	$CDCl_3$	2.08(s,$C_6\underline{Me}_6$)		6.40(H_2O)

Table 1.3 (contd.)

Compound	Solvent	δ η-arene	δ acetate	δ other
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2(PPh_3)$	$CDCl_3$	2.17(s, $C_6\underline{Me}_6$)	1.93[b]	7.33(PPh_3)
$Ru(\eta\text{-}C_6Me_6)(O_2CCF_3)_2(PPh_3)$	CD_2Cl_2	1.79(s, $C_6\underline{Me}_6$)		7.4(PPh_3)
$Ru(\eta\text{-}C_6H_6)Cl_2(NCOH.C_2H_2S)$	d^6-DMSO	6.05(s)		6.65(d, 7Hz)[c] 8.80(d, 7Hz) 2.88(OH)
$Ru(\eta\text{-},4\text{-}MeC_6H_4CHMe_2)Cl_2(NCOHC_2H_2S)$	$CDCl_3$	5.60, 5.41(AB Pattern, $C_6\underline{H}_4$), J 6Hz), 3.04(sp, $C\underline{H}Me_2$), 2.18(s, Me), 1.31(d, $CHMe_2$, J 7Hz)		6.52(d, 7Hz)[c] 8.51(d, 7Hz) 3.48(OH)

a Chemical shifts (δ) in ppm relative to internal TMS. Chemical shifts measured in CD_3NO_2 (δ4.33), d^6-DMSO (δ2.62) and CD_3CN (δ2.00) were referenced to the residual proton resonances of the respective solvents.

b An additional peak at δ1.98 of unknown origin was also present.

c Doublets due to olefinic C<u>H</u> of isothiazoline ligand.

Table 1.4 IR spectra (400-150 cm^{-1}) of arene ruthenium(II) carboxylates[a]

$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(O_2CMe)$	308(vs)[b], 297(vs)[c], 269(w),228(m),209(sh),203(s),179(s)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Br(O_2CMe)$	302(s)[b], 270(wbr), 203(mbr),163(m)
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$	309(vs)[b], 295(sh)[c], 237(s),225(s),193(m),168(mbr)
$Ru(\eta\text{-}C_6Me_6)Br(O_2CMe)$	302(s)[b], 270(w),223(s),188(mbr),158(mbr)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl()_2CCF_3)$	395(wbr),320-310(wbr),290-280(mbr),220(w)
$Ru(\eta\text{-}C_6Me_6)Cl(O_2CCF_3)$	384(w),280(s),270(sh),208(s),193(sh),164(mbr)
$Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(O_2CMe)_2$	395(wbr)[d], 307(vs)[b], 289(s),270(sh),227(m),220-200(mbr),183(s)
$Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$	384(s)[d], 308(vs br)[b], 294(vs br),272(s),242(m),210(m),164(s)

[a] Spectra run as polythene discs

[b] ν(Ru-OCOMe)(bidentate)

[c] ν(Ru-Cl)

[d] ν(Ru-OCOMe)(unidentate)

Table 1.5 ^{1}H N.m.r., ν(Ru-Cl) and conductivity data for arene ruthenium(II) and osmium(II) complexes

Compound	Solvent	δ η-arene	δ other	ν(Ru-Cl) (cm^{-1})	Conductivity ($Scm^2\ mol^{-1}$)
$[Ru(\eta\text{-}C_6H_6)Cl(pyz)_2][PF_6]$	CD_3NO_2	6.10(s,$C_6\underline{H}_6$)	8.72(m)(pyz)	299	75
$[Ru(\eta\text{-}C_6H_6)Cl(4,4'\text{-bipy})_2][BPh_4]$	CD_3NO_2	5.93(s,$C_6\underline{H}_6$)	8.67(m),7.61(m)(bipy)[a]	285(br)	49
$[Ru(\eta\text{-}C_6H_6)Cl(\underline{m}\text{-dithiane})_2][PF_6]$	CD_3NO_2	6.07(s,$C_6\underline{H}_6$)	3.25(m),2.92(m),2.33(m) ($\underline{m}$-dithiane)		
$\{RuCl_2(\eta\text{-},4\text{-}MeC_6H_4CHMe_2)\}_2(\mu\text{-pyz})$	CD_3NO_2	5.66,5.40(AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 8Hz), 3.05(sp,$C\underline{H}Me_2$), 2.21(s,Me), 1.35(d,$CH\underline{Me}_2$, $\underline{J}$ 7Hz)	9.10(s)(pyz)	290	0
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$	CD_3NO_2	6.05,5.78(AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 10Hz), 2.79(sp,$C\underline{H}Me_2$), 1.88(s,Me), 1.15(d,$CH\underline{Me}_2$, $\underline{J}$ 7Hz)	8.82(m)(pyz)	296	85
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(pyz)_2][PF_6]$	CD_3NO_2	6.28,6.08(AB pattern, $C_6\underline{H}_4$, $\underline{J}$ 9Hz), 1.93(s,Me) 1.19(d,$CH\underline{Me}_2$, $\underline{J}$ 7Hz)[b]	8.67(m)(pyz)[c]	298	79
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(\underline{m}\text{-dithiane})_2][BPh_4]$	CD_3NO_2	6.05(s,$C_6\underline{H}_4$), 2.28(s,Me), 1.31(d,$CH\underline{Me}_2$, $\underline{J}$ 7Hz)	3.28(m),2.86(m) ($\underline{m}$-dithiane)	292	48

[a] Overlapping with peaks due to $[BPh_4]^-$ at δ6.8-7.7 [b] Septet due to $C\underline{H}Me_2$ not observed [c] Overlapping AB patterns

Table 1.6 $^{13}C-\{^{1}H\}$ N.m.r. data at 301 K for selected compounds in CD_3NO_2[e]

Compound	η-arene	other
[h,g,a] $[(\eta\text{-}C_6Me_6)Ru(OCOCH_3)_2]H_2O$	88.30($\underline{C}_6Me_6$) 15.71($C_6(\underline{C}H_3)_6$)	24.30($O_2C\underline{C}H_3$) 182.77($O_2\underline{C}CH_3$)
[a] $[(\eta\text{-}C_6H_6)RuClpyz_2][PF_6]$	86.4	147.84, 146.50
[f,b] $[(\eta\text{-p-cymene})OsClpyz_2][PF_6]$	95.44(A) 92.91(B) 79.90(C) 73.98(D) 29.71(E) 20.16(F) 15.38(G)	147.32, 147.09
[c,f] $[(\eta\text{-p-cymene})OsCl(\text{m-dithiane})_2][BPh_4]$	105.17(A) 96.75(B) 82.00(C) 78.47(D) 32.08(E) 22.55(F) 18.35(G)	30.75,30.07,29.30,27.92 [d](166.64, 137.26, 127.19, 123.30)
[b,f] $[(\eta\text{-p-cymene})RuClpyz_2][PF_6]$	104.54(A) 101.65(B) 87.14(C) 82.51(D) 29.86(E) 20.37(F) 15.83(G)	147.54, 146.56
[c,f] $(\eta\text{-p-cymene})RuCl_2(NCOHC_2H_2S)$	103.92(A) 97.77(B) 82.52(C) 82.52(C) 81.77(D) 30.63(E) 22.03(F) 18.28(G)	171.94 ($\underline{C}OH$) 150.83 ($HOC\underline{C}H$) 111.98 ($S\underline{C}H$)

[a] Recorded on XL-100 A

[b] Recorded on WH360

[c] Recorded on CFT20

[d] Due to carbons of $[BPh_4]^-$

[e] Chemical shifts quoted to high frequency of T.M.S.

[g] Spectrum recorded in $CDCl_3$

[h] at 208 K peaks shift to 88.72, 15.13 and 25.51 ppm respectively

[f] labelling of p-cymene signal

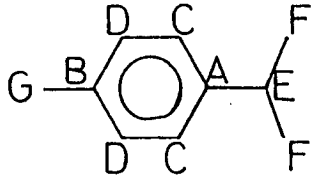


Table 1.7 Atomic Coordinates for $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_4N_2)_2][PF_6]$

No.	Atom	Fractional coordinates x 10^4 [a]		
		X	Y	Z
1	Ru1	8183 (1)	-1969(09)	-2963(07)
2	Cl1	10254 (3)	-2153 (3)	-4593 (2)
3	N4	11876(16)	-941(11)	-1146(14)
4	C5	11889(19)	-344 (7)	-2065(13)
5	C6	10851(14)	-652(13)	-2606(10)
6	N1	9831(10)	-1590 (9)	-2182 (7)
7	C2	9791(15)	-2174(13)	-1230(10)
8	C3	10870(17)	-1835(16)	-720(13)
9	N4'	8988(12)	-6961(11)	-2042 (9)
10	C5'	9888(16)	-6335(15)	-2912(11)
11	C6'	9722(14)	-4937(13)	-3165(10)
12	N1'	8610 (9)	-4124 (8)	-2573 (7)
13	C2'	7691(14)	-4732(13)	-1694(10)
14	C3'	7887(16)	-6130(15)	-1456(11)
15	C10	6639(12)	-395(11)	-1956 (9)
16	C21	5936(11)	-1654(11)	-1825 (9)
17	C31	5803(11)	-2336(10)	-2745 (8)
18	C40	6402(12)	-1743(11)	-3795 (9)
19	C30	7130(12)	-502(11)	-3893 (9)
20	C20	7256(12)	185(12)	-3002 (9)
21	C50	6825(14)	254(13)	-980(10)
22	C70	6687(15)	-4002(13)	-4749(11)
23	C60	6214(13)	-2476(12)	-4780 (9)
24	C71	4690(18)	-2191(18)	-4875(14)
25	P1	6572 (5)	-3968 (5)	1573 (3)
26	F1	8236(12)	-4276(11)	822 (9)
27	F2	6215(13)	-2997(12)	659(10)
28	F3	4899(13)	-3763(12)	2320 (9)
29	F6	7093(16)	-2829(15)	2135(12)
30	F5	6061(12)	-5218(11)	1047 (8)
31	F4	6897(12)	-5042(11)	2447 (9)

Table 1.7 (contd.)

		Fractional coordinates x 10^4		
No.	Atom	X	Y	Z
32	H5	12685(19)	439(17)	-2044(13)
33	H6	10833(14)	-150(13)	-3378(10)
34	H2	8948(15)	-2906(13)	-857(10)
35	H3	10853(17)	-2139(16)	74(13)
36	H5'	10785(16)	-6959(15)	-3443(11)
37	H6'	10522(14)	-4488(13)	-3863(10)
38	H2'	6791(14)	-4107(13)	-1166(10)
39	H3'	7099(16)	-6584(15)	-752(11)
40	H21	5499(12)	-2119(11)	-1026 (9)
41	H31	5238(11)	-3292(10)	-2638 (8)
42	H30	7610(12)	-50(11)	-4691 (9)
43	H20	7817(12)	1144(12)	-3115 (9)
44	H51	7897(14)	713(13)	-1326(10)
45	H52	6792(14)	-227(13)	-200(10)
46	H53	5917(14)	1049(13)	-886(10)
47	H701	7838(15)	-4261(13)	-4741(11)
48	H702	6530(15)	-4351(13)	-5482(11)
49	H703	5920(15)	-4351(13)	-4060(11)
50	H60	6794(13)	-1891(12)	-5523 (9)
51	H711	4185(18)	-1153(18)	-4725(14)
52	H712	3972(18)	-2920(18)	-4337(14)
53	H713	4814(18)	-2427(18)	-5701(14)

[a] Esd's in parenthesis

Table 1.8 Selected Bond Distances and Angles for the Cation $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl(C_4H_4N_2)_2]^+$

The e.s.d.'s in bond lengths are all less than 0.02 Å and in bond angle are generally less than 1.0°

(a) Distances (Å)

Ru(1)-Cl(1)	2.41	N(1)-C(2)	1.38
Ru(1)-N(1)	2.18	N(1)-C(6)	1.34
Ru(1)-N(1)'	2.15	C(2)-C(3)	1.44
Ru(1)-C(10)	2.21	C(3)-N(4)	1.30
Ru(1)-C(20)	2.20	N(4)-C(5)	1.29
Ru(1)-C(21)	2.18	C(5)-C(6)	1.41
Ru(1)-C(30)	2.17	N(1)'-C(2)'	1.34
Ru(1)-C(31)	2.19	N(1)'-C(6)'	1.32
Ru(1)-C(40)	2.21	C(2)'-C(3)'	1.38
C(10)-C(50)	1.51	C(3)'-N(4)'	1.33
C(40)-C(60)	1.52	N(4)'-C(5)'	1.33
C(60)-C(70)	1.49	C(5)'-C(6)'	1.38
C(60)-C(71)	1.55		

(b) Angles (°)

N(1)-Ru(1)-Cl(1)	86	C(70)-C(60)-C(71)	110
N(1)-Ru(1)-N(1)'	86	Ru(1)-N(1)-C(2)	121
N(1)'-Ru(1)-Cl(1)	89	Ru(1)-N(1)-C(6)	120
C(21)-C(10)-C(30)	121	C(2)-N(1)-C(6)	118
C(20)-C(10)-C(50)	119	N(1)-C(2)-C(3)	120
C(20)-C(10)-C(21)	119	N(1)-C(6)-C(5)	121
C(10)-C(21)-C(31)	121	C(2)-C(3)-N(4)	121
C(10)-C(20)-C(30)	119	C(3)-N(4)-C(5)	120
C(20)-C(30)-C(40)	123	N(4)-C(5)-C(6)	121
C(21)-C(31)-C(41)	120	Ru(1)-N(1)'-C(2)'	120
C(30)-C(40)-C(31)	118	Ru(1)-N(1)'-C(6)'	124
C(30)-C(40)-C(60)	121	C(2)'-N(1)'-C(6)'	116
C(31)-C(40)-C(60)	121	N(1)'-C(2)'-C(3)'	121
C(40)-C(60)-C(70)	114	N(1)'-C(6)'-C(5)'	122
C(40)-C(60)-C(71)	108	C(2)'-C(3)'-N(4)'	124
		C(3)'-N(4)'-C(5)'	114
		N(4)'-C(5)'-C(6)'	123

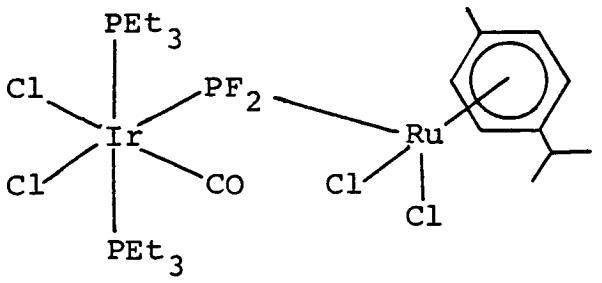
CHAPTER 2

The Preparation, Characterisation and Some Reactions of Binuclear and Tetranuclear η-arene Ruthenium(II) Complexes

2.1 Introduction

In recent years there has been considerable interest in binuclear η-arene-ruthenium(II) complexes. This interest has been stimulated by the fact that several of these complexes have been shown to be useful catalyst precursors for a variety of processes. Most of the binuclear species reported to date are cationic[75,76] in nature containing halide, hydroxide, alkoxide or hydride bridges, although a few neutral bridged species have also been synthesised. This introduction summarises the chemistry of the previously reported bridged species and discusses their role in a variety of catalytic processes.

Except for the neutral di-bridged species $[Ru(\eta\text{-arene})X_2]_2$ (X = Cl, Br, I) which are the precursors to all the materials discussed herein, there are few other examples of neutral, bridged η-arene-ruthenium(II) systems[4,77]. One bimetallic species worth mentioning however is that obtained on reacting $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ with $[Ir(CO)Cl_2(PEt_3)_2PF_2]$[78] in toluene. The product of this reaction has been characterised by X-ray crystallography as $[Ir(CO)Cl_2(PEt_3)_2PF_2Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]$[79] (28) and a similar reaction has been observed between the iridium complex and $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ or $[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$[80]. In these reactions the iridium complexes can be regarded as a novel type of difluorophosphine ligand since the reaction is of the simple cleavage type described in Chapter 1.



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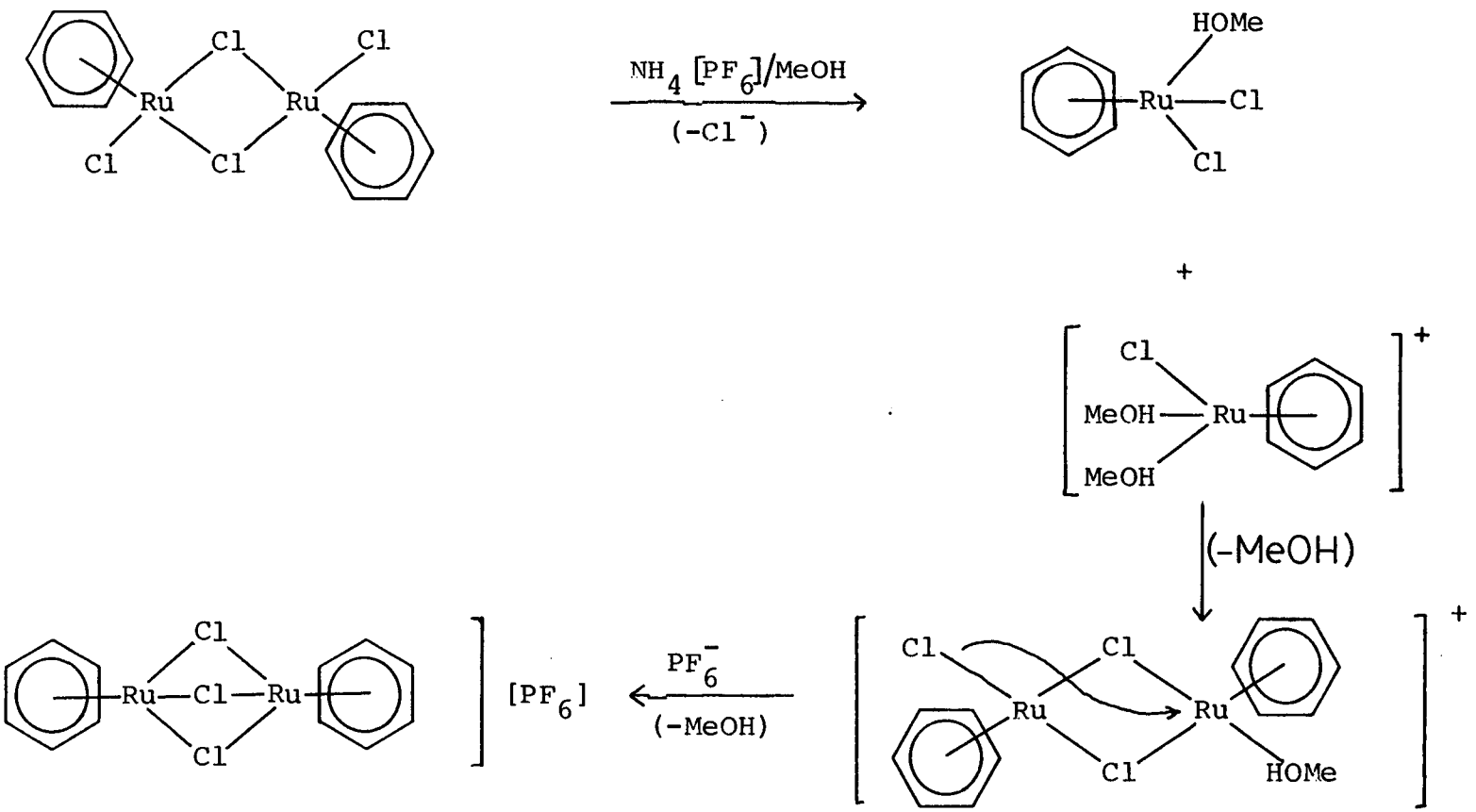
Most of the remaining complexes are of the mono-cationic triple bridged type, although several examples of dicationic dibridged species have also been reported.

The first triple bridged η-arene-ruthenium(II) compound to be reported was $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]PF_6$ which was prepared from $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ and NH_4PF_6 in water[5]. Subsequent work showed that this compound could be isolated in significantly higher yield by reaction in methanol[10]. Unfortunately, it was not possible to prepare the analogous triple bromo- and iodo- species by this route. This failure has been attributed to the fact that the precursors to these complexes were too insoluble in methanol for sufficient concentrations of the solvated monomers, postulated as the reaction intermediates (see Scheme 2.1) to be generated, and hence the failure to form the triple halo bridged cations.

Scheme 2.1 A possible mechanism for the formation of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][PF_6]$



A more general route to these triple bridged species has been described[9]. Thus reaction of $Ru(\eta\text{-arene})X_2(C_5H_5N)$ and $[Ru(\eta\text{-arene})X(C_5H_5N)_2][PF_6]$ (arene = C_6H_6, X = Cl, Br; arene = 1,3,5-$C_6H_3Me_3$, X = Cl, I) (1:1 molar ratio) with HBF_4 in methanol gives in high yield the triple bridged complexes $[Ru_2(\eta\text{-arene})_2X_3][BF_4]$. The role of the fluoroboric acid in these reactions is to protonate the pyridine ligands, thus labilising them and allowing the formation of the weakly methanolated monomers proposed as intermediates in Scheme 2.1. These then couple forming a triple bridged cationic product. Evidence that this reaction may involve a solvated, double halide bridged intermediate is provided by the observation that reaction of $[Ru(\eta\text{-1,4-Me}C_6H_4CHMe_2)X_2]_2$ (X = Cl, Br, I) with $AgPF_6$ (1:1 molar ratio) in acetone gives $[Ru_2(\eta\text{-1,4-Me}C_6H_4CHMe_2)_2X_3][PF_6]$ in reasonable yield[9]. Interestingly it has been shown that the triple bridged cation $[M_2(\eta\text{-arene})_2X_3]^+$ (M = Ru, X = Br, arene = 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl, arene = C_6H_6) can be generated, in low yield, from HBF_4 and $[M(\eta\text{-arene})X(C_5H_5N)_2][PF_6]$ alone, probably by a pathway involving fast halide exchange. This presumably generates some of the neutral species $M(\eta\text{-arene})X_2(C_5H_5N)$ which can then couple to form the triple bridged species[9].

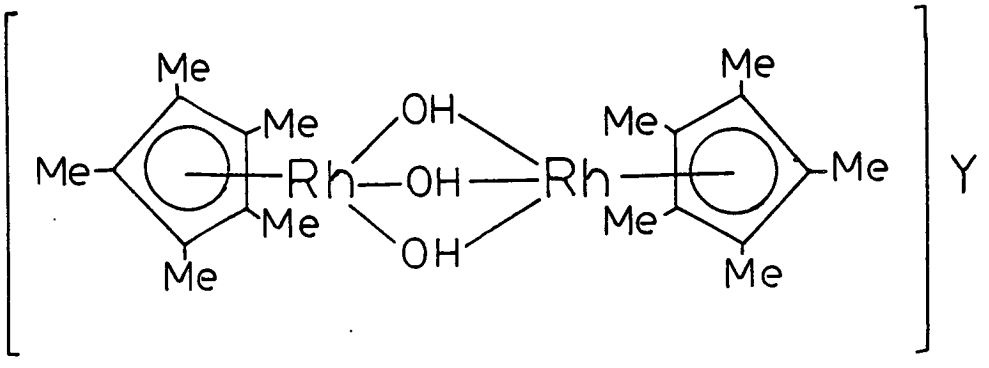
Attempts to generate heterobridged complexes, analogous to the molybdenum complex, $[Mo_2(\eta^7\text{-}C_7H_7)_2ClBr_2]$ [81], by reaction of $Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)$ and $[Ru(\eta\text{-}C_6H_6)Br\text{-}(C_5H_5N)_2][PF_6]$ with HBF_4 in methanol have been reported to give statistical mixture of the $-(\mu\text{-}Cl)_3-$, $-(\mu\text{-}Cl)_2(\mu\text{-}Br)-$, $-(\mu\text{-}Cl)(\mu\text{-}Br)_2$ and $-(\mu\text{-}Br)_3-$ cations [9].

Similarly attempts to generate the hetero-arene complex $[Ru_2(\eta\text{-}C_6H_6)(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl_3][BF_4]$ by reaction of an equimolar mixture of $Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_5N)$ and $[Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl(C_5H_5N)_2][PF_6]$ with HBF_4 in methanol results not only in the formation of the desired product but also in the formation of some $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$ and $[Ru_2(\eta\text{-}C_6H_3Me_3)_2Cl_3][BF_4]$. A statistical mixture of these three products has also been obtained by mixing equimolar amounts of the $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ and $[Ru_2(\eta\text{-}C_6H_2Me_3)_2Cl_3]^+$ cations in solution [9]. Finally a hetero-metallic species $[RuOs(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$ has been observed as a component of the mixture obtained upon reacting $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$ with $[Os_2(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$. Reaction pathways have been proposed [9] for the various processes described above.

In solution these triple halide bridged cations undergo a variety of bridge cleavage reactions with the production of monomeric species. For example, $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][PF_6]$ was found to react in alcohols with various Lewis bases (L) to give the cationic complexes

$[Ru(\eta\text{-}C_6H_6)Cl(L)_2][PF_6]$ and the neutral compounds $Ru(\eta\text{-}C_6H_6)Cl_2L$, (L = PPh_3, $AsPh_3$, SEt_2, C_5H_5N etc.)[82].

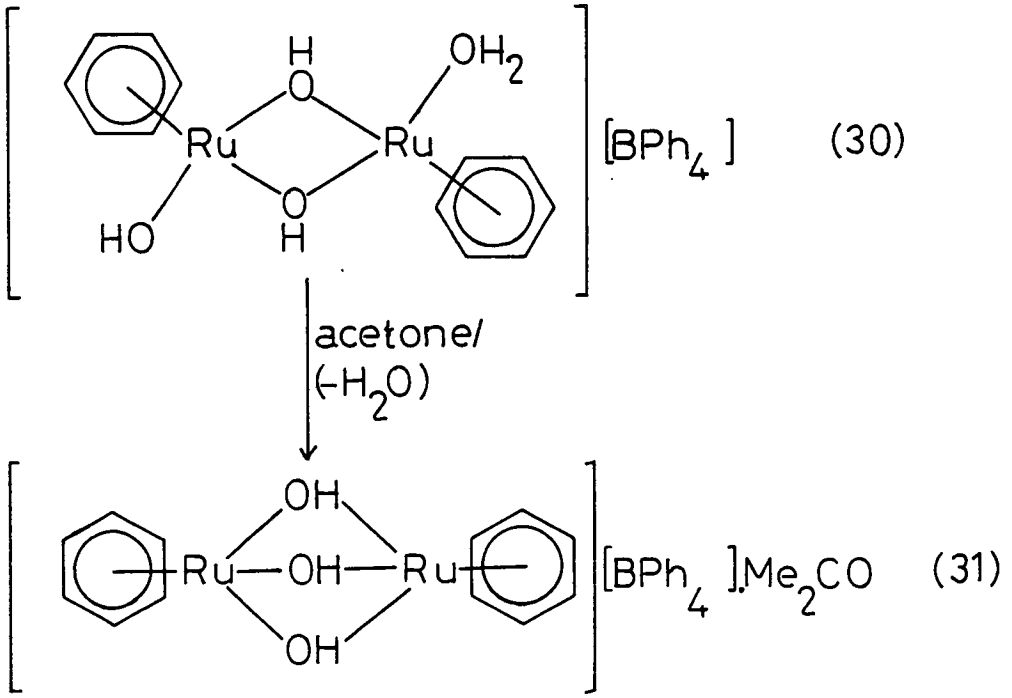
Kang and Maitlis synthesised the stable tri-μ-hydroxo complex $[Rh_2(\eta^5\text{-}C_5Me_5)_2(OH)_3][Y]$ (29) (Y = Cl) by reaction of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ with aqueous sodium hydroxide[57]. The binuclear triple-μ-hydroxo structure was subsequently confirmed by X-ray analysis for Y = BPh_4[75] and OH.11 H_2O[83]. Other workers have extended this reaction to prepare the isoelectronic η-arene ruthenium(II) complexes.



(29)

The initial product formed upon reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of aqueous sodium hydroxide or sodium carbonate, and subsequent treatment with $NaBPh_4$, was not the triple bridged species but a mixture of two binuclear complexes[68,82,84]. The major product has been postulated as the di-μ-hydroxo bridged cation, $[(\eta\text{-}C_6H_6)(OH)Ru(OH)_2Ru(H_2O)(\eta\text{-}C_6H_6)]^+$ (30),

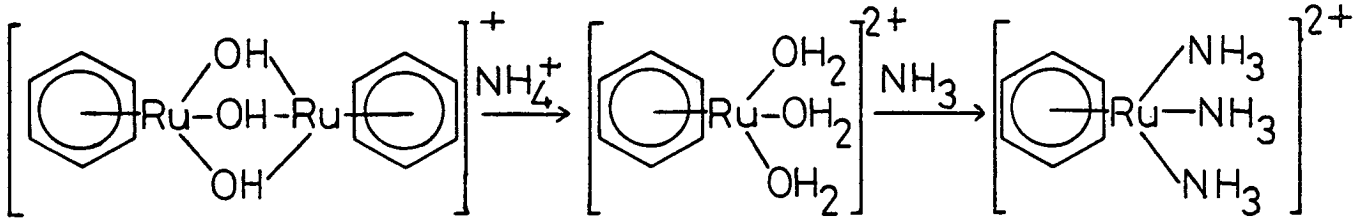
while the minor product was claimed to be the genuine tri-μ-hydroxo cation $[(\eta\text{-}C_6H_6)Ru(OH)_3Ru(\eta\text{-}C_6H_6)]^+$ (31). Upon recrystallisation from acetone (30) is converted to (31) (Equation 6) and the only compound obtained was "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3][BPh_4]$.acetone". However, a further examination of this reaction, the results of which will be discussed fully later in this Chapter, has shown that (31) should be reformulated as the novel tetranuclear dication, $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$. Similar observations to those discussed above have been made for the reaction of $[Os(\eta\text{-}C_6H_6)Cl_2]_2$ with sodium hydroxide. In contrast reaction of other $[Ru(\eta\text{-arene})Cl_2]_2$ with an excess of aqueous sodium hydroxide or sodium carbonate gave only the $[Ru_2(\eta\text{-arene})_2(OH)_3]^+$ cations[68] and the presence of the $-Ru(OH)_3Ru-$ bridging unit in the latter complexes has been verified by a preliminary crystal structure determination of the complex $[Ru_2(1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl.3H_2O$[88].



.....[6]

If the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with sodium carbonate is carried out using only a 1:1 molar ratio of $[Ru^{2+}]:[CO_3^{2-}]$, in the presence of an excess of sulphate ion, then an orange crystalline solid is obtained. This has been shown by X-ray analysis to be the novel tetrameric species $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$[11,89]. The factors influencing the formation of this species, the details of the crystal structure determination and some reactions of the complex will be discussed later in this Chapter.

Attempts to isolate the $[PF_6]^-$ salts of the cations (30) and (31) by addition of $NH_4[PF_6]$ did not yield the expected product. On standing for several days a yellow crystalline material was deposited from solution. This material has been formulated as $[Ru(\eta\text{-}C_6H_6)(NH_3)_3][PF_6]_2$[15]. The mechanism of formation of this trisamine complex has been postulated as involving protonation of the bridging hydroxyl groups by ammonium ion, subsequent bridge cleavage to form a trisaqua intermediate, $[Ru(\eta\text{-}C_6H_6)(H_2O)_3]^{2+}$, which then undergoes stepwise substitution by ammonia ligands (Equation [7]). Similar mechanisms involving protonation and cleavage steps will be proposed later in this chapter, for a variety of protonation reactions of "$[Ru_2(\eta\text{-arene})_2(OH)_3]^+$" cations.

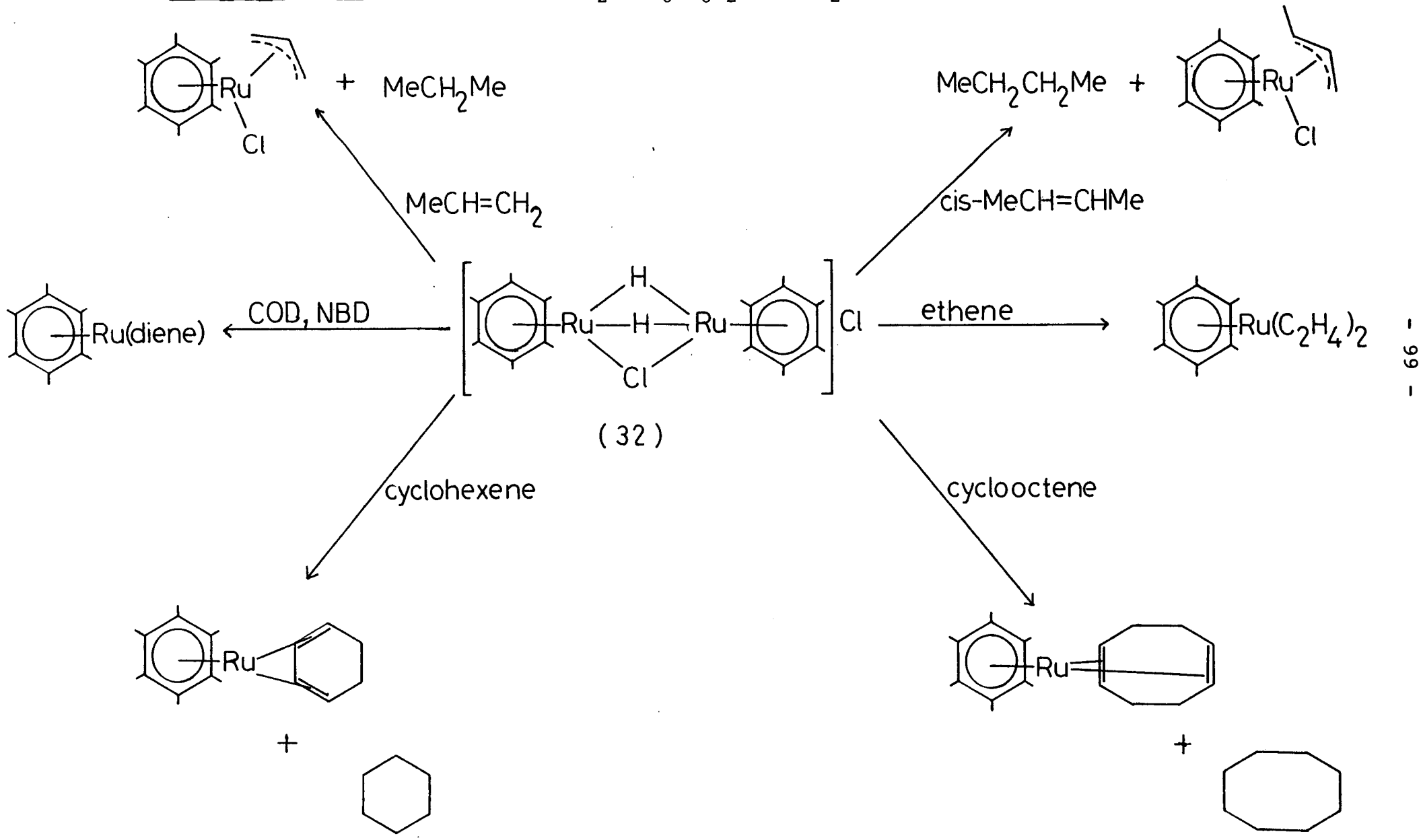


.....[7]

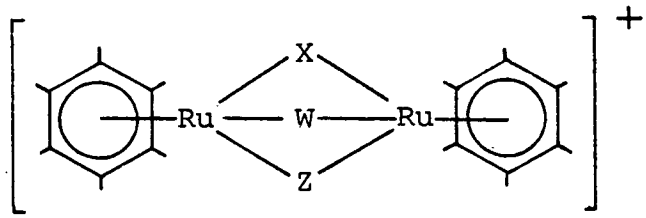
The reaction of "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3][BPh_4].Me_2CO$" with methanol under reflux produces a product which no longer contains hydroxide ligands and this has been formulated as the tri-μ-methoxo complex $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ [68]. Similarly, reaction in ethanol produces the corresponding $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$. These reactions are believed to proceed <u>via</u> a protonation mechanism similar to that described above, although the monomeric species generated are now presumed to take part in a coupling reaction to form the binuclear cation. The same products have also been synthesised by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with NaOR in ROH (R = Me, Et). Reaction with longer chain alcohols has been shown to result in extensive decomposition. This reaction has been successfully extended to the synthesis of a variety of $[M_2(\eta\text{-arene})_2(OMe)_3][BPh_4]$ complexes (M = Ru, arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6; M = Os, arene = C_6H_6), as discussed later in this chapter.

Several hydrido-arene ruthenium(II) complexes have been reported, a number of which have been found to be catalytically active. Thus, reaction of the η-hexamethylbenzene complex $Ru(\eta\text{-}C_6Me_6)Cl_2(PPh_3)$ under a variety of conditions gives the air-sensitive yellow complex $Ru(\eta\text{-}C_6Me_6)H(Cl)PPh_3$ [29]. This complex has also been reported to be formed in the reaction of $[Ru_2(\eta\text{-}C_6Me_6)_2(Cl)(H)_2]Cl$ (32) with PPh_3 and the latter complex was prepared by reaction of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ with aqueous sodium carbonate in propan-2-ol [90]. Complex (32) undergoes a variety of reactions with olefins to form initially enyl or η^3-allyl ruthenium(II) complexes, several of which then eliminate HCl to form dieneruthenium(0) complexes (Scheme 2.2). Subsequent work has shown that treatment of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ in propan-2-ol with aqueous 1 molar sodium carbonate (1 mol per mol of dimer) gives the red mono-μ-hydrido complex $[Ru_2(\eta\text{-}C_6Me_6)_2(H)(Cl)_2]Cl$ whereas the reaction of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ with 2 moles of sodium carbonate per mole of dimer gives a complex mixture of products among which the di-μ-hydride $[Ru_2(\eta\text{-}C_6Me_6)_2(Cl)(H)_2]Cl$ and tri-μ-hydride $[Ru_2(\eta\text{-}C_6Me_6)_2(H)_3]Cl$ can be identified [30]. The latter can also be prepared by reduction of (32) with ethanolic $Na[BH_4]$. However, if the η-mesitylene complex, $[Ru(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cl_2]_2$, is treated with aqueous sodium carbonate in propan-2-ol, only the tri-μ-hydride complex $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(H)_3]Cl$ is isolated [90].

Scheme 2.2 The reactions of $[Ru_2(\eta\text{-}C_6Me_6)_2(Cl)(H)_2]Cl$ with olefins



Several μ-hydrido areneruthenium(II) complexes have been generated by reaction with propan-2-ol at elevated temperatures, from the areneruthenium(II) carboxylates $Ru(\eta\text{-arene})(O_2CR)_2$ and $Ru(\eta\text{-arene})Cl(O_2CR)$ (R = Me, CF_3), discussed in Chapter 1[30]. Thus $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ gives rise to $[Ru_2(\eta\text{-}C_6Me_6)_2(O_2CMe)_2(H)][H(O_2CMe)_2]$ (33a) whereas $Ru(\eta\text{-}C_6Me_6)Cl(O_2CMe)$ gives the salts $[Ru_2(\eta\text{-}C_6Me_6)_2(H)(O_2CMe)(Cl)][Y]$ (Y = $Cl.2H_2O$, PF_6) (33b). When the reaction is carried out using less highly substituted arenes, then mixtures of hydrido complexes are reported to be formed, but subsequent treatment with $NH_4[PF_6]$ usually precipitates out the mono-μ-hydrido complex.



(33)

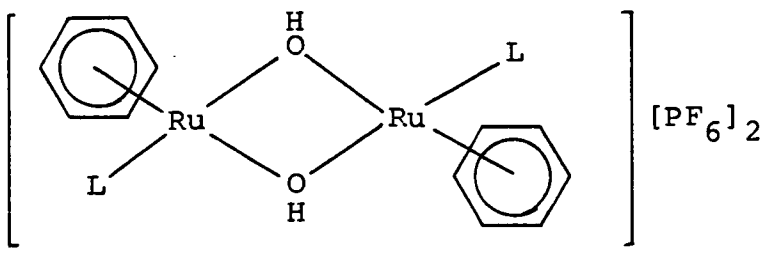
a, X = W = O_2CMe, Z = H

b, X = O_2CMe, W = H, Z = Cl

In all the reactions described above it is the species containing the arenes with the greatest degree of permethylation which are the most stable. For example, there are no reports of stable η -benzene ruthenium(II) hydrido complexes.

Few dicationic bridged species are known but it has been shown that reaction of the tetrameric,

$[\{Ru(\eta\text{-}C_6H_6)OH\}_4]^{4+}$ cation, with Lewis bases, L (L = C_5H_5N, γ-picoline), gives the dicationic $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_2L_2][PF_6]_2$ (34)[89] which contains a double μ-hydroxo bridging unit.



(34)

As mentioned earlier several of the complexes discussed in this introduction and in the first chapter have been found to be active catalyst precursors for a variety of processes. In general the most extensively studied reaction is that involving hydrogenation of an unsaturated moiety. Since the discovery by Iguchi[85a] in 1939 that certain rhodium(III) complexes will catalyse the reduction by hydrogen of organic substrates, much effort has been devoted to finding more efficient homogeneous hydrogenation catalysts.

In most proposed mechanisms the unsaturated substrate is first activated by coordination to the metal centre and subsequently hydrogen transfer from the metal to the substrate takes place. Normally the protic source is molecular hydrogen, which may add by an oxidative, homolytic or heterolytic mechanism, or it may be supplied by a donor molecule such as an alcohol. In several cases both types

of mechanism have been found to operate for the one catalyst. For example the mononuclear hydride $Ru(\eta\text{-}C_6Me_6)HCl(PPh_3)$ is a stable long lived, homogeneous catalyst for the hydrogenation of benzene and a variety of olefins with molecular hydrogen and is also on active catalyst for the transfer hydrogenation of olefins by secondary alcohols[29].

Under relatively mild conditions, (50°C, 50 atmos. of H_2), low concentrations of this complex will catalyse the hydrogenation of benzene to cyclohexane. As no cyclohexadienes or cyclohexene can be detected either during or after the reaction, then we can conclude that the benzene must remain strongly complexed to the active intermediate throughout the hydrogenation process†

This complex also shows high activity for catalysing hydrogen transfer from secondary alcohols to olefins. Unlike $RhH(PPh_3)_4$ and $RuH_2(PPh_3)_4$[86,87], which only catalyse the reaction with mono-olefins, $Ru(\eta\text{-}C_6Me_6)HCl(PPh_3)$ catalyses transfer hydrogenation of both mono and poly-olefins such as cyclo-octa-1,3-diene, cyclo-octa-1,5-diene and cyclo-octatetraene.

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†In a recent communication the catalyst $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_6H_6)]^{2+}$ was reported to be active for the selective hydrogenation of benzene to cyclohexene[85b].

To date, the majority of arene ruthenium(II) complexes which have been examined for catalytic activity are binuclear species. It has been shown that complex (32) is the most stable and active catalyst so far discovered for homogeneous hydrogenation of arenes to cyclohexanes[90]. These reactions do not require the presence of a co-catalyst, in contrast to the closely related $[Rh_2(\eta^5\text{-}C_5Me_5)_2Cl_2]_2\text{-}Et_3N$ system. Furthermore the turnover rate for the reduction of benzene to cyclohexane is more than five times that found using, under similar conditions, the monomeric species discussed above. This catalyst is also useful in that it will selectively hydrogenate the aromatic rings of methylbenzoate, anisole and phenol without producing appreciable hydrogenolysis of the functional group.

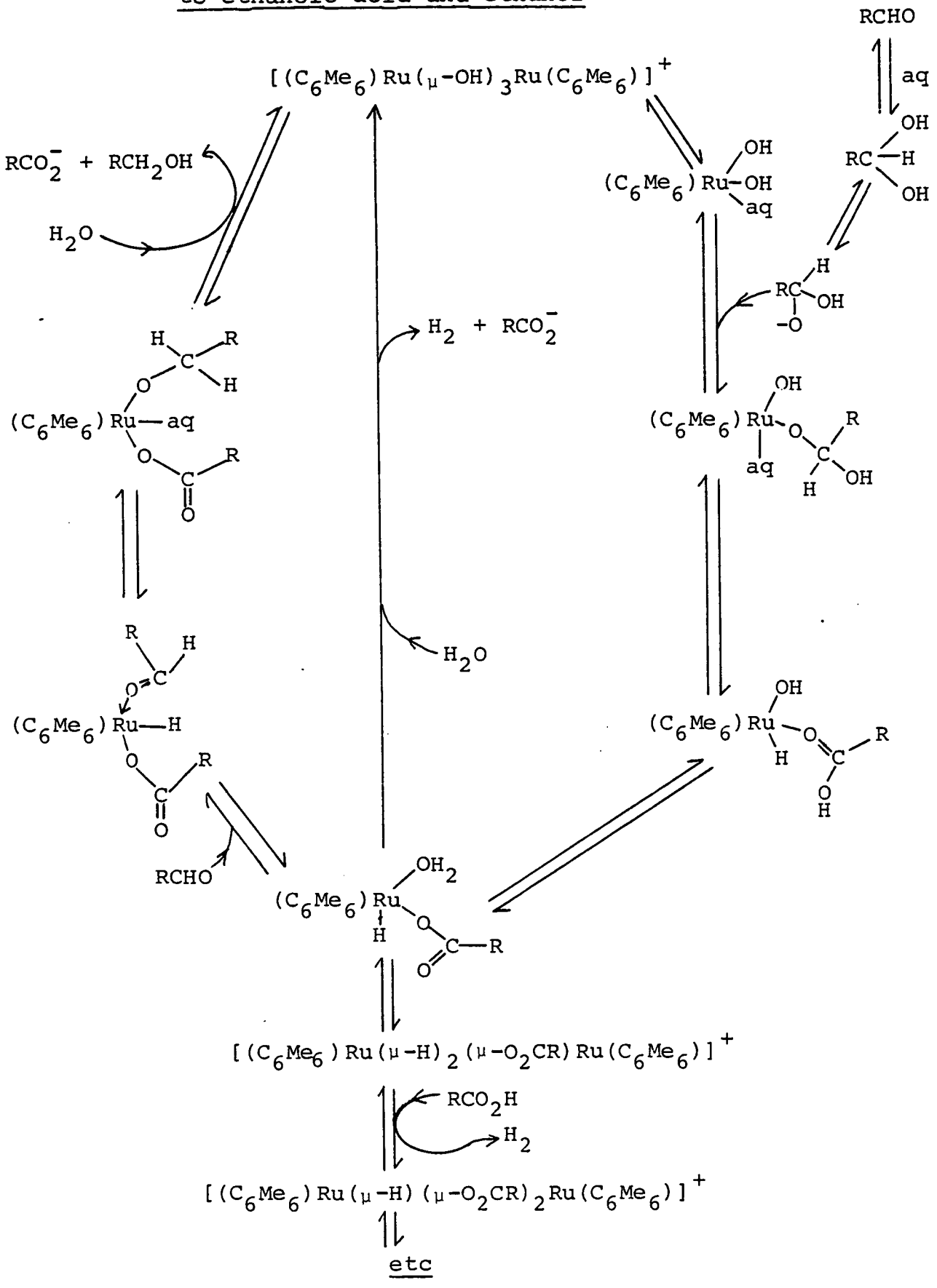
However, it has been reported that hydrogenolysis does occur with diphenylether and halobenzenes and that nitrobenzene is readily reduced to aniline. Studies made on the mono and tri-μ-hydrido species $[Ru_2(\eta\text{-}C_6Me_6)_2\text{-}H(Cl)_2]Cl$ and $[Ru_2(\eta\text{-}C_6Me_6)_2(\eta\text{-}H)_3]Cl$ have shown that although both are active catalysts for the hydrogenation of benzene to cyclohexane, both are clearly less active than either $Ru(\eta\text{-}C_6Me_6)HCl(PPh_3)$ or (32)[30].

It has also been shown that a variety of ruthenium(II) complexes are active catalysts for the disproportionation of ethanal to ethanoic acid and ethanol[60]. The catalytic

reaction proceeds slowly under neutral or acidic conditions but the rate of reaction is greatly increased under basic conditions. These reactions have been demonstrated to be viable both in aqueous and mixed aqueous-organic media, thus allowing studies to be made which involve catalysts or aldehydes which are only soluble in organic solvents. Work on the catalytic properties of the isoelectronic $[M_2(\eta^5\text{-}C_5Me_5)_2(OH)_3]Y$ (M = Rh, Y = $Cl.4H_2O$, $OH.11H_2O$; M = Ir, Y = $OH.xH_2O$, $O_2CMe.14H_2O$) systems have shown that ethanoic acid and ethanol are produced in approximately equimolar amounts[60]. However, the ruthenium complexes $[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Y$ (Y = $Cl.4H_2O$, $PF_6.2H_2O$) generally give significantly greater amounts of ethanoic acid. One of the advantages of homogeneous catalysis is that the catalysts may be fine-tuned to give a specific product. Thus addition of tertiary phosphines, pyridine or dimethylsulphoxide to the reaction mixture inhibits the formation of the carboxylic acid, but not the alcohol.

A mechanism has been proposed for this aldehyde disproportionation reaction (Scheme 2.3) and kinetic studies indicate that the reaction is first order in aldehyde and half-order in the binuclear metal catalyst[60]. This indicates that the catalytically active species is probably a mononuclear species formed in a rate-determining pre-equilibrium dissociation step. The carboxylic acid formed

Scheme 2.3 The catalytic disproportionation of ethanal to ethanoic acid and ethanol (60)



in the reaction has been shown to react further with one of the intermediates to form binuclear species. In the rhodium system a variety of mixed bridged species have been isolated, e.g. $[Rh_2(\eta^5\text{-}C_5Me_5)_2H(O_2CR)_2][PF_6]$ and $[Rh_2(\eta^5\text{-}C_5Me_3)_2H(OH)(O_2CR)][PF_6]$ (R = H, Et, Ph), whereas if the catalyst precursor is $[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]^+$ then the only product isolated is the tri-μ-carboxylato species $[Ru_2(\eta\text{-}C_6Me_6)_2(O_2CMe)_3][PF_6]$. This is probably due to the fact that the ruthenium hydrides generated are too labile, under the prevalent reaction conditions, to be detected and indeed molecular hydrogen is evolved in the course of the reaction[60].

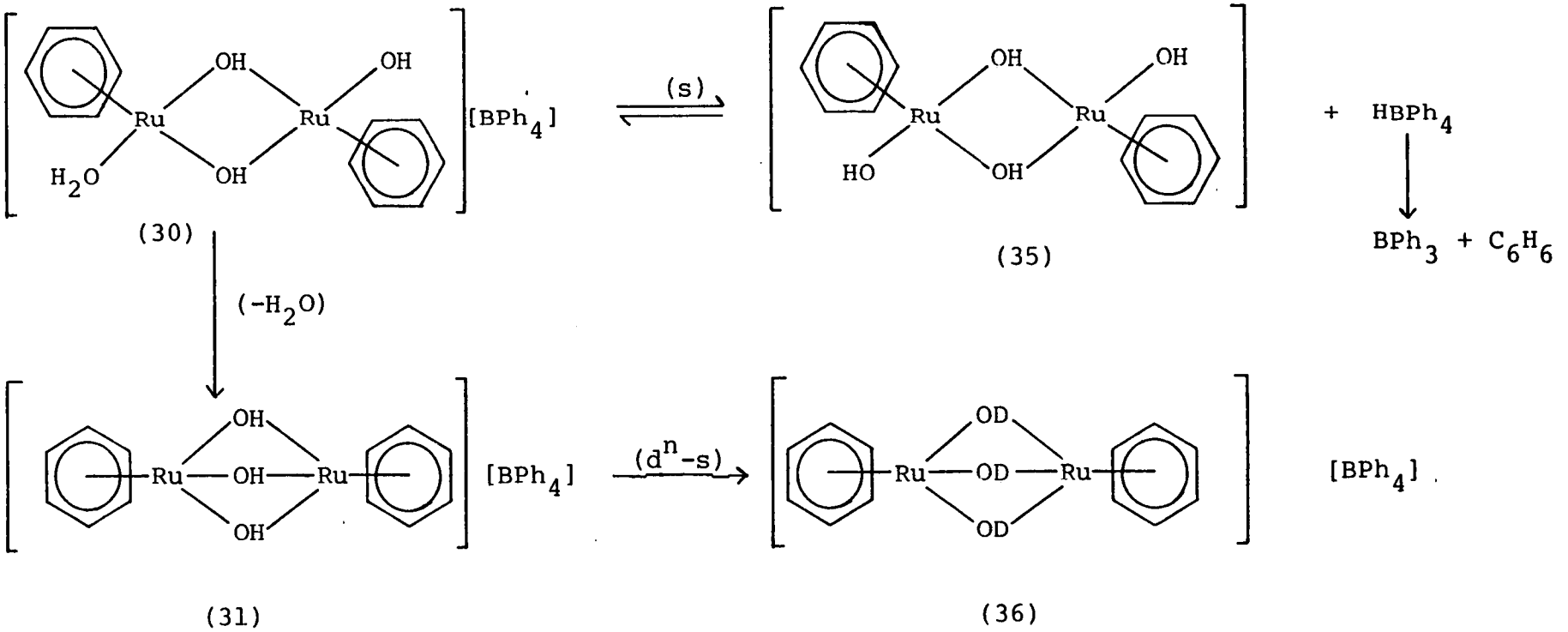
Obviously the results discussed here are only preliminary forays into the field of areneruthenium(II) catalysts and there must undoubtedly be much scope for further investigations into this and other catalytic processes, such as carbonylation, hydroformylation, oligomerization, etc.

2.2 A reinvestigation of the products formed in the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of aqueous NaOH or Na_2CO_3: the x-ray crystal structure determination of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$

The initial product formed from the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of NaOH or Na_2CO_3 in water, isolated as its $[BPh_4]^-$ salt, shows two ν(OH) vibrations at 3615 cm^{-1} and 3520 cm^{-1} with a shoulder at 3530 cm^{-1} in its mull infrared spectrum. On recrystallisation from acetone only one ν(OH) stretch at 3530 cm^{-1} was observed. The ^1H n.m.r. spectrum in $(CH_3)_2CO$ at 298 K of this initial product shows a major resonance at δ5.33 ppm, with a second weak peak at 5.56 ppm, in CD_3NO_2 the resonances appear at δ5.40 and 5.57 ppm respectively, and both are attributed to π-bonded benzene. The resonance at 5.57 ppm in CD_3NO_2 grows on ageing of the solution and an orange precipitate forms in the tube. This precipitation occurs more rapidly in $(CD_3)_2CO$. The precipitate was shown to be a deuterated complex by infra-red spectroscopy which showed bands at ca. 2600 cm^{-1} attributable to ν(OD) vibrations. The compound recrystallised from acetone showed two resonances in the same positions as previously, but the relative intensities are now reversed, with the major resonance now at δ5.57 ppm. The ^1H n.m.r. spectrum of the initial product was originally interpreted as arising from a mixture of the cations[82] $[Ru_2(\eta\text{-}C_6H_6)_2(OD)_3]^+$ (δ = 5.40 ppm) and $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]^+$ (δ = 5.57 ppm) but since the

deuterated complexes are precipitated from solution and the initial major resonance is at 5.40 ppm, this explanation seemed unlikely. In addition a separation of ca. 0.2 ppm between the two η-C_6H_6 resonances would seem to be unusually large. A better interpretation of this result may be that the signals arise from a neutral complex, $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_4]$ (35), and a mono-cationic complex $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ (30)[84]. It was postulated that the latter complex would be readily deprotonated in solution to form (35) and $HBPh_4$. However, the latter species would be expected to decompose to BPh_3 and benzene and as this process was not observed, then this explanation also seems unlikely. The most plausible explanation advanced to date is that the major product formed initially is the double bridged cation (30) which then eliminates water to form the triple bridged complex (31)[68]. Conductivity measurements over a concentration range have shown that the initial product was a 1:1 electrolyte, while a single measurement on the recrystallised product was also consistent with a 1:1 electrolyte (Λ_m(10^{-3} M in CH_3NO_2 at 298 K) = 55 S cm^2mol^{-1}). Since there are two different η-benzene environments it might have been expected that the resonance at δ5.40 ppm would be split at low temperature but this was not found to be the case[84]. The various interpretations previously postulated are summarised in Scheme 2.4.

Scheme 2.4 Some possible interpretations of the products formed in the Reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of NaOH or Na_2CO_3



(s = Me_2CO or $MeNO_2$)

The true identity of the recrystallised product has now been determined by X-ray analysis.

Crystal Structure of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$

Details of the solution of the structure are given in the experimental section. Final atomic parameters are given in Table 2.3 and selected bond distances and angles in Table 2.4. Contrary to expectations the cation was not binuclear but rather a novel tetranuclear dication, $[Ru_4(\eta\text{-}C_6H_6)_4(\mu\text{-}OH)(\mu_4\text{-}O)]^{2+}$ (see Figure 2.1). This can be thought of as two binuclear units which share one common bridging vertex. The two Ru...Ru vectors are orthogonal and hence the geometry about the four coordinate bridging oxygen is distorted tetrahedral. Only a few examples of tetrahedrally coordinated oxygen in discrete coordination complexes are known, notably in the beryllium compounds $Be_4O(O_2CR)_6$ and in some zinc complexes[91a], and this appears to be the first example in transition metal chemistry, although a closely related complex $[Rh_3(\eta\text{-}C_5Me_5)_3H_3(O)][PF_6].H_2O$, obtained from $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]^+$ and hydrogen in isopropanol, has been reported[91b]. The coordination about each ruthenium ion is octahedral with the η-benzenes occupying these adjacent coordination sites. The Ru-Ru distance across a binuclear unit is 3.004(3) Å and the separation between non triple bridged metal ions lie in the range 3.65-3.71 Å, thus precluding any direct metal-metal bonding interaction. None of the Ru-C distances

are significantly different from the mean value of 2.19 Å and the metal to ring centroid distances all lie within the normal range of 1.62-1.68 Å. The Ru-O distances vary between 2.04 and 2.15 Å (see Table 2.4), but there is no significant difference between the lengths of bonds to the four coordinate oxygen and bonds to the bridging hydroxyl groups. The internal Ru-O-Ru angles all lie between 90 and 94°. The external Ru-O(5)-Ru angles have an average value of 120°. Thus the geometry about the four coordinate oxygen is far from that of an idealised tetrahedron. The presence of two acetone molecules of solvation may be important in helping to stabilise this unusual structure as the close approach of O(6) and O(7) to the bridging hydroxyls O(3) and O(4) (O(3)-O(6) 2.88 Å, O(4)-O(7) 2.84 Å) is indicative of a hydrogen bonding interaction between these groups. The structure does not show any other close intermolecular contacts.

The structure of the cation is shown in Figure 2.1, an ORTEP diagram of the central "Ru_4O_5" unit in Figure 2.2 and a cell packing diagram in Figure 2.3.

Although the structure of the recrystallised product has been unequivocally determined in the solid state, it is still possible that in solution the complex exists as a triply bridged binuclear species. If however the ^1H n.m.r. spectrum of the recrystallised product is recorded in a sealed n.m.r. tube in CD_3NO_2, which has been freshly

Figure 2.1 The molecular structure of the cation $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$

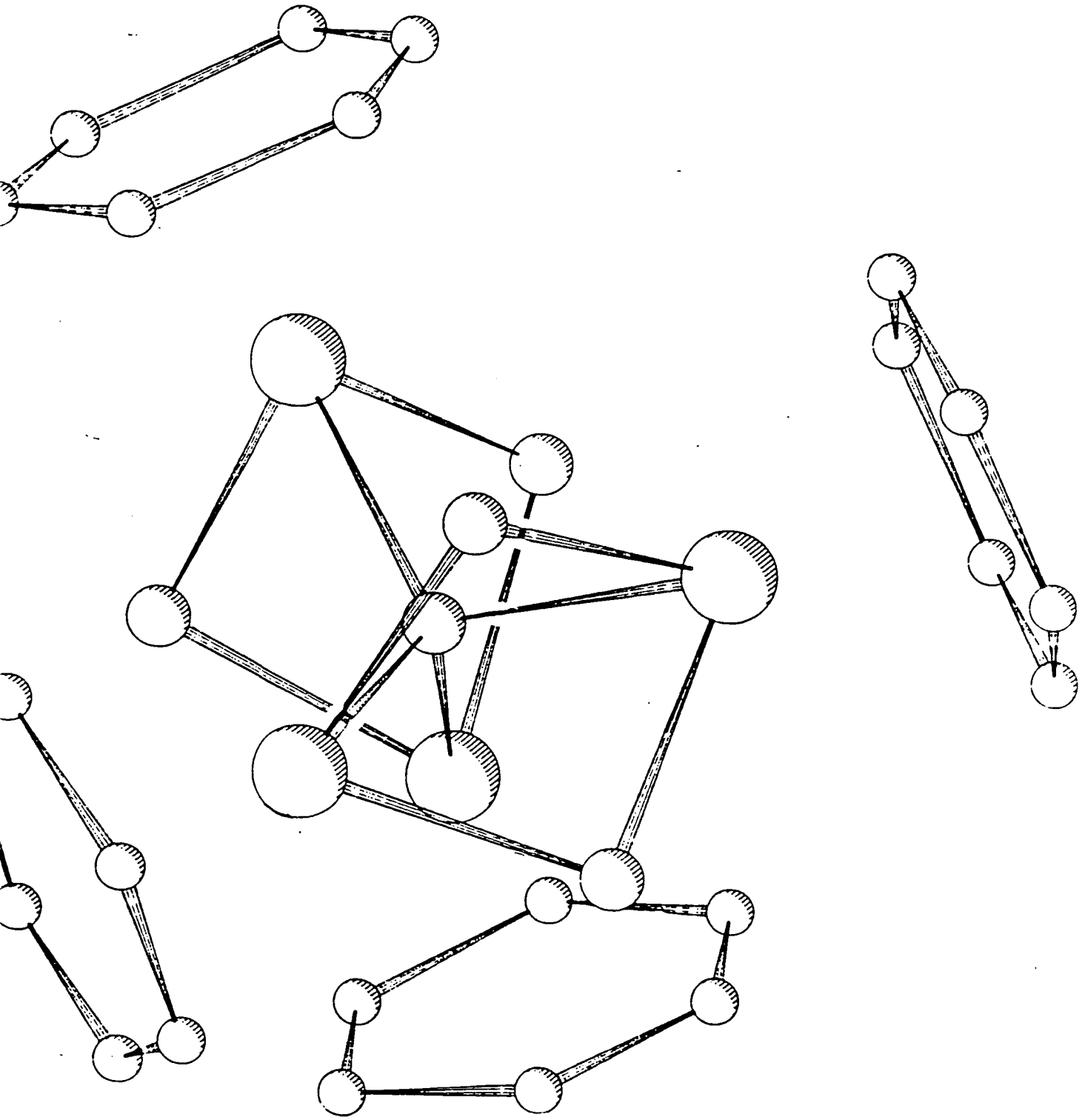


Figure 2.2 An ORTEP plot of the central "Ru_4O_5" unit

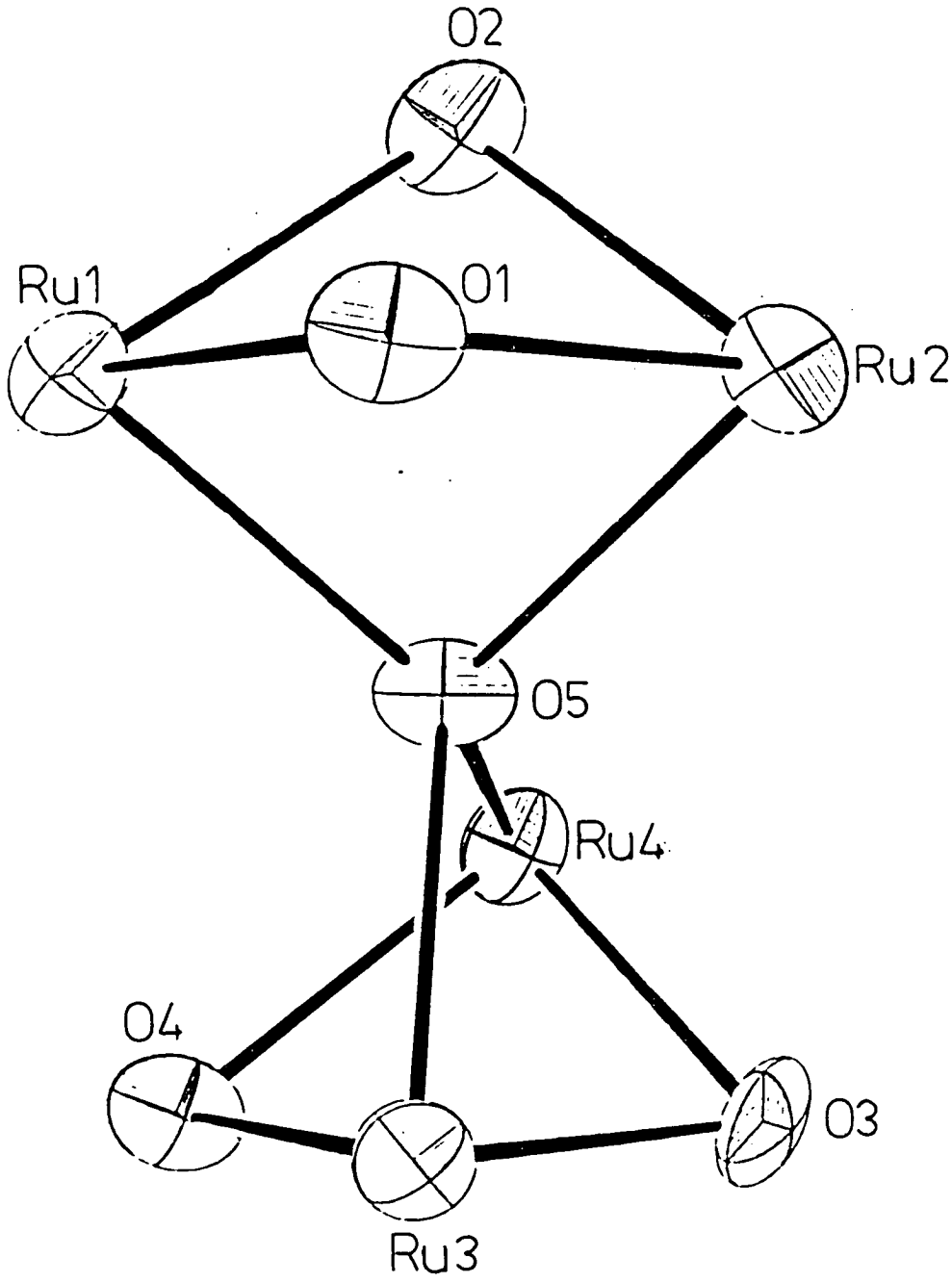
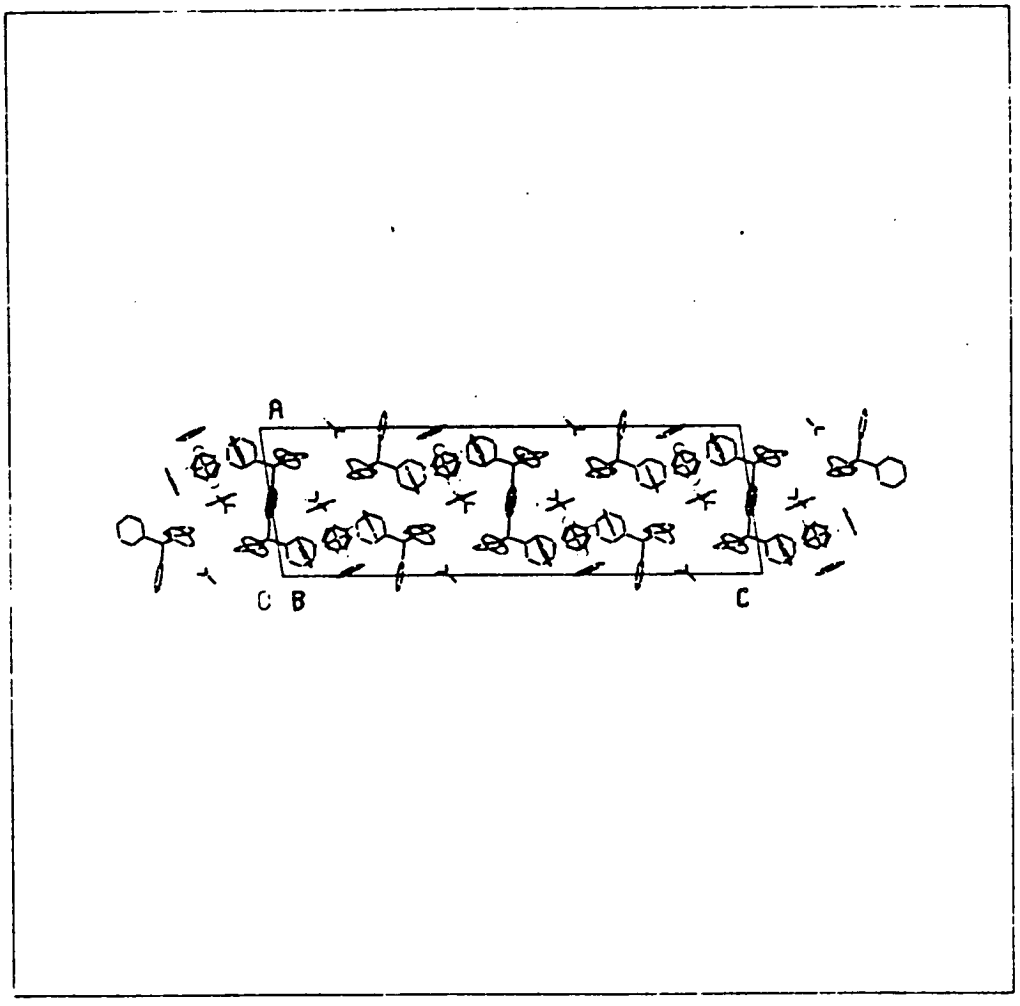


Figure 2.3 A cell packing diagram for $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$



distilled from P_2O_5, then only one resonance is observed, at δ5.57 ppm. On opening the n.m.r. tube and introducing a small amount of water, a second resonance immediately starts to grow, at δ5.40 ppm, at the expense of the original signal. After a period of 24 hours the ratio of the two signals is ca. 1:6 i.e. the spectrum is identical to that of the unrecrystallised product formed initially. In addition the different positive charges on the cations now accounts for the 0.2 ppm separation of the η-C_6H_6 resonances. The facile hydration of a tetrahedrally coordinated oxygen atom has also been observed for the zinc complexes mentioned previously, although the oxygen atom in $Be_4O(O_2CR)_6$ resists hydration. Further evidence for the solid state structure being retained for some time in solution comes from a study of conductance measurements made over a concentration range. In freshly distilled nitromethane, a molar conductivity Λ_m = 116 S cm^2 mol^{-1}, for a 10^{-3} mol dm^{-3} solution is obtained and a plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ gives a straight line of slope 630 which is consistent with that expected for a 2:1 electrolyte[92].

The mechanism of formation of this unusual dication need not be all that different from the mechanism previously postulated for the formation of the binuclear cation (see Equation [6]). The latter involved intramolecular loss of a water molecule[68], whereas for the formation of the tetranuclear dication, an intermolecular loss of water is proposed as the initial

step (see Scheme 2.5). Proton transfer to one of the terminal hydroxyl groups may then take place and subsequent attack by the oxygen results in the stepwise displacement of two water molecules and the formation of the tetranuclear dication.

This result would have cast doubt on the existence of the triple hydroxo-bridged areneruthenium(II) complexes claimed by various workers were it not for the fact that the crystal structure determination of $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl.3H_2O$ has unequivocally shown that this complex is binuclear[88] (see Figure 2.4). The Ru-Ru, Ru-O and Ru-C distances of 2.99, 2.11 and 2.19 Å are very similar to those reported for the tetranuclear benzene dication. A possible explanation for the different nature of these products may lie in the fact that the ring with no aliphatic substituents can pack more compactly and hence increase crystal stability, whereas in the case of substituted benzenes a similar tetranuclear structure would result in severe steric crowding. Hence intramolecular elimination of water from the $[Ru_2(\eta\text{-arene})_2(OH)_3(H_2O)]^+$ intermediates is apparently favoured for substituted benzenes.

Scheme 2.5 A possible mechanism for the formation of the $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ dication (n.b. benzene rings omitted for clarity)

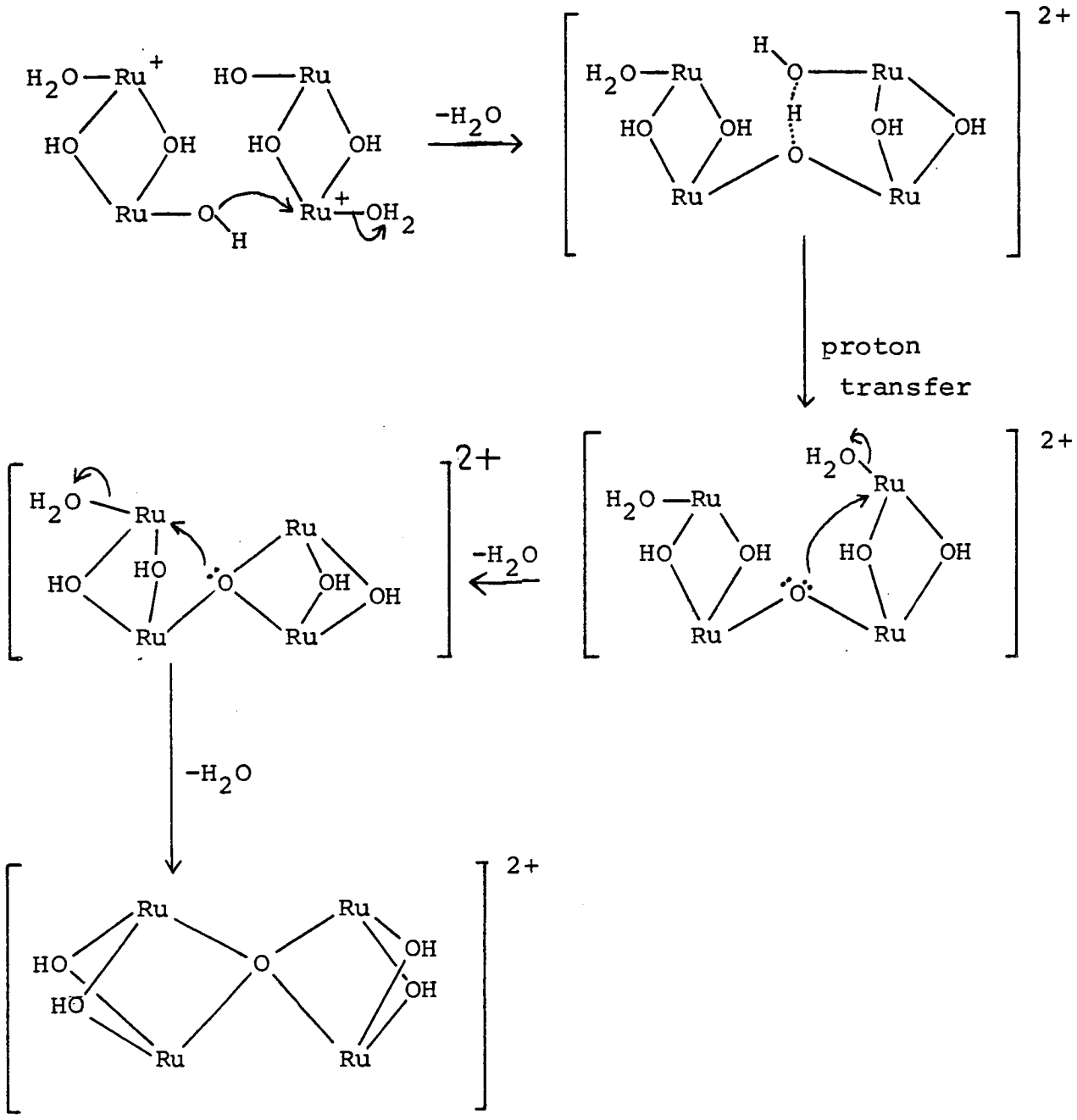
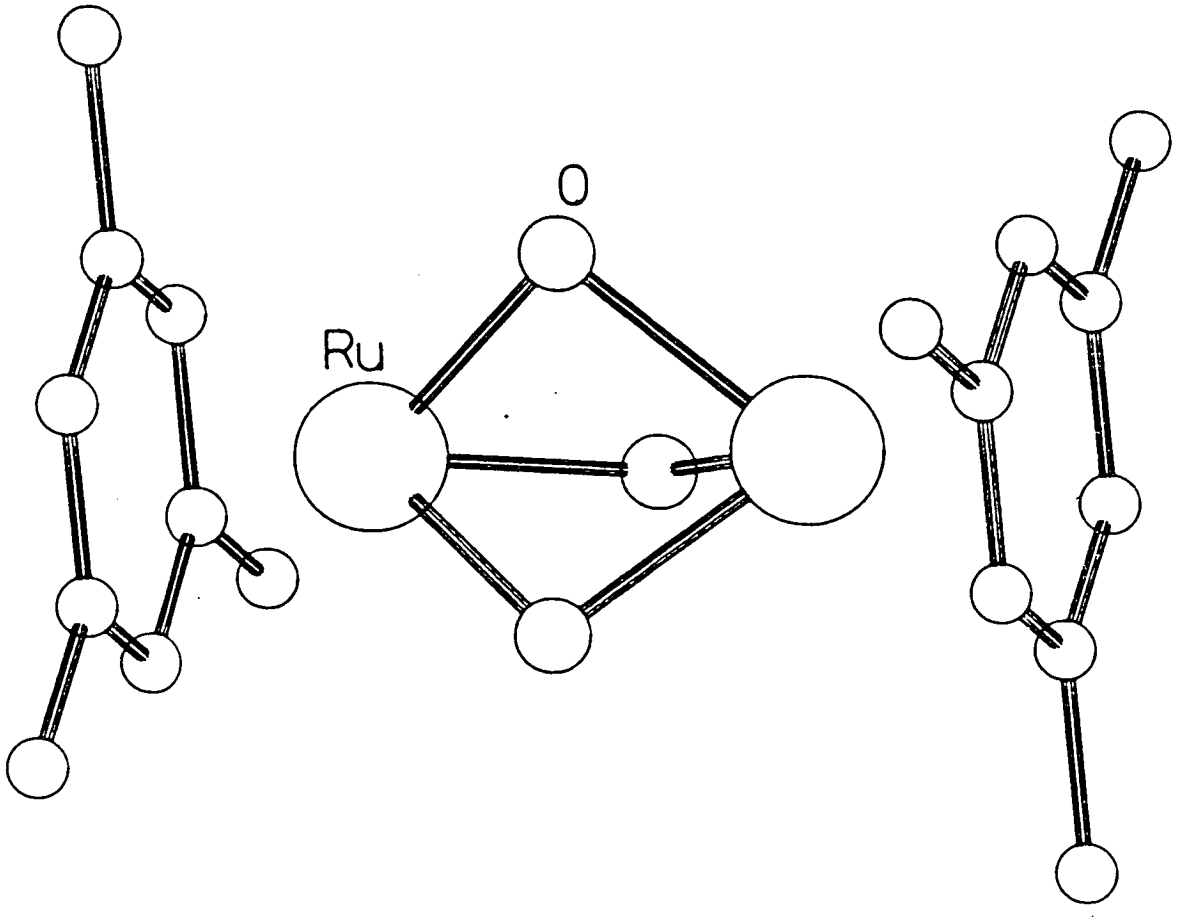


Figure 2.4 The molecular structure of the cation $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]^+$



2.3 The preparation, X-ray crystal structure analysis and some reactions of the hydroxo-bridged, tetranuclear η-arene ruthenium(II) quadrivalent cation $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$

The complexes described in the previous section were obtained by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of aqueous NaOH or Na_2CO_3. If however, $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ is dissolved in water and shaken with a large excess of Na_2SO_4 for a short period and this solution then treated with Na_2CO_3, ($[Ru^{2+}]:[CO_3^{2-}]$ *ca.* 1:1 molar ratio), an orange crystalline solid is deposited in low yield. Without the addition of Na_2CO_3 no precipitate is obtained even upon prolonged interaction. The yield of the compound can be increased by pretreating an aqueous solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with $AgNO_3$ and after filtering off the AgCl, shaking with an excess of Na_2SO_4 followed by Na_2CO_3 (in 1:2 molar ratio).

The orange crystalline material is too insoluble in organic solvents for ^1H n.m.r. studies and is not sufficiently volatile for mass spectral studies. The infrared spectrum of the product showed broad bands at *ca.* 3250 and 1640 cm^{-1} assigned to ν(OH) and ν(HOH) vibrational modes of water, which obscure bands arising from ν(OH) of any hydroxyl groups. No bands due to ν(RuCl) vibrations are observed but bands at 1060, 975, 610 and 478 cm^{-1} suggest that the sulphate ion[93] is present in the complex. A strong band at 864 cm^{-1} indicates that the benzene ring had been retained.

The complex was sparingly soluble in water and gave strongly conducting solutions, but addition of $Na[BPh_4]$ to the aqueous solution gives a precipitate which rapidly decomposed on standing.

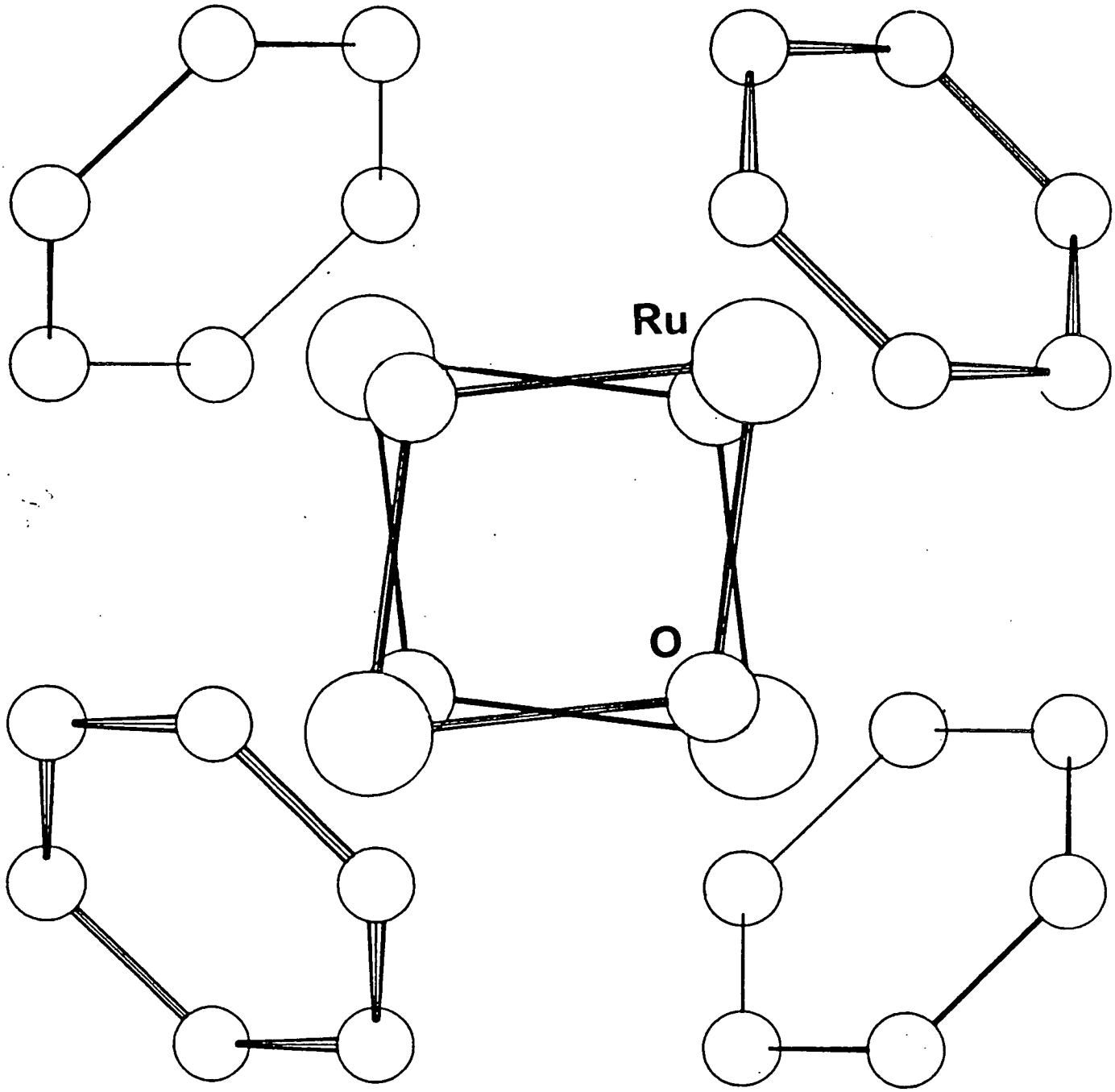
Elemental analysis of the complex confirmed the presence of C, H, O and S and the absence of chlorine, and suggested the empirical formula $C_{12}H_{26}O_{12}Ru_2S$, which together with the physical and spectroscopic properties described above are consistent with the molecular formula $[Ru(\eta\text{-}C_6H_6)(OH)]_{2n}[SO_4]_n.6nH_2O$. An X-ray structural analysis (see below) shows the complex to be $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$ which once again contains a tetranuclear cation with π-bonded benzenes and hydroxyl bridging ligands.

Crystal structure of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$

Details of the solution of the structure are given in the experimental section and final atomic parameters in Table 2.5. The coordination about the ruthenium atom is octahedral with an η-benzene ring and three hydroxyl groups. The Ru-O distance in the "cube" is 2.117(7) Å and the angles at Ru and O are 75.8(1)° and 102.6(2)° respectively. The metal to ring centroid distance is 1.62 Å which is less than that found for the cation $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$, and the Ru-C distance is 2.151(8) Å. The C-C distance in the rings is 1.395(10) Å. The benzene rings are disordered about two positions related by a 30° rotation about a threefold axis.

This tetrameric cation is only the second ruthenium complex with this cubane stereochemistry ($[Ru_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}CO)_4]$ is the other[94]) and the first example of a cubane-like structure containing π-bonded arene rings, although a large number of cubane clusters containing a wide range of elements, with different bridging and terminal groups are known[95]. The molecular structure of the cation is shown in Figure 2.5. Attempts to synthesise other $[\{Ru(\eta\text{-arene})(OH)\}_4]^{4+}$ cations by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$, 1,4-$MeC_6H_4CHMe_2$) with stoichiometric amounts of Na_2CO_3 in the presence of an excess of Na_2SO_4 in water were unsuccessful since only unreacted starting materials and/or hydroxo bridged cations $[Ru_2(\eta\text{-arene})_2(OH)_3]^+$ were recovered on work-up. For example, reaction of $[Ru(\eta\text{-1,3,5-}C_6H_3Me_3)Cl_2]_2$ with aqueous $AgNO_3$ followed by shaking with an excess of Na_2CO_4 and then Na_2CO_3 (1:2 molar ratio) for several hours gave on concentration, the triple hydroxo bridged complex $[Ru_2(\eta\text{-1,3,5-}C_6H_3Me_3)_2(OH)_3][NO_3].H_2O$. Attempts to exchange the hydroxo bridging ligands of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{2+}$ for alkoxo ligands, with retention of the tetrameric structure, by reaction with MeOH at elevated temperatures gave only the well known cation $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$. Finally attempts to synthesise a chloro-bridged analogue, $[\{Ru(\eta\text{-}C_6H_6)Cl\}_4]^{4+}$, by reaction of $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_5N)_2][PF_6]$ with $BF_3.Et_2O$ was also unsuccessful as a mixture of four products, (^1H n.m.r. evidence), was obtained.

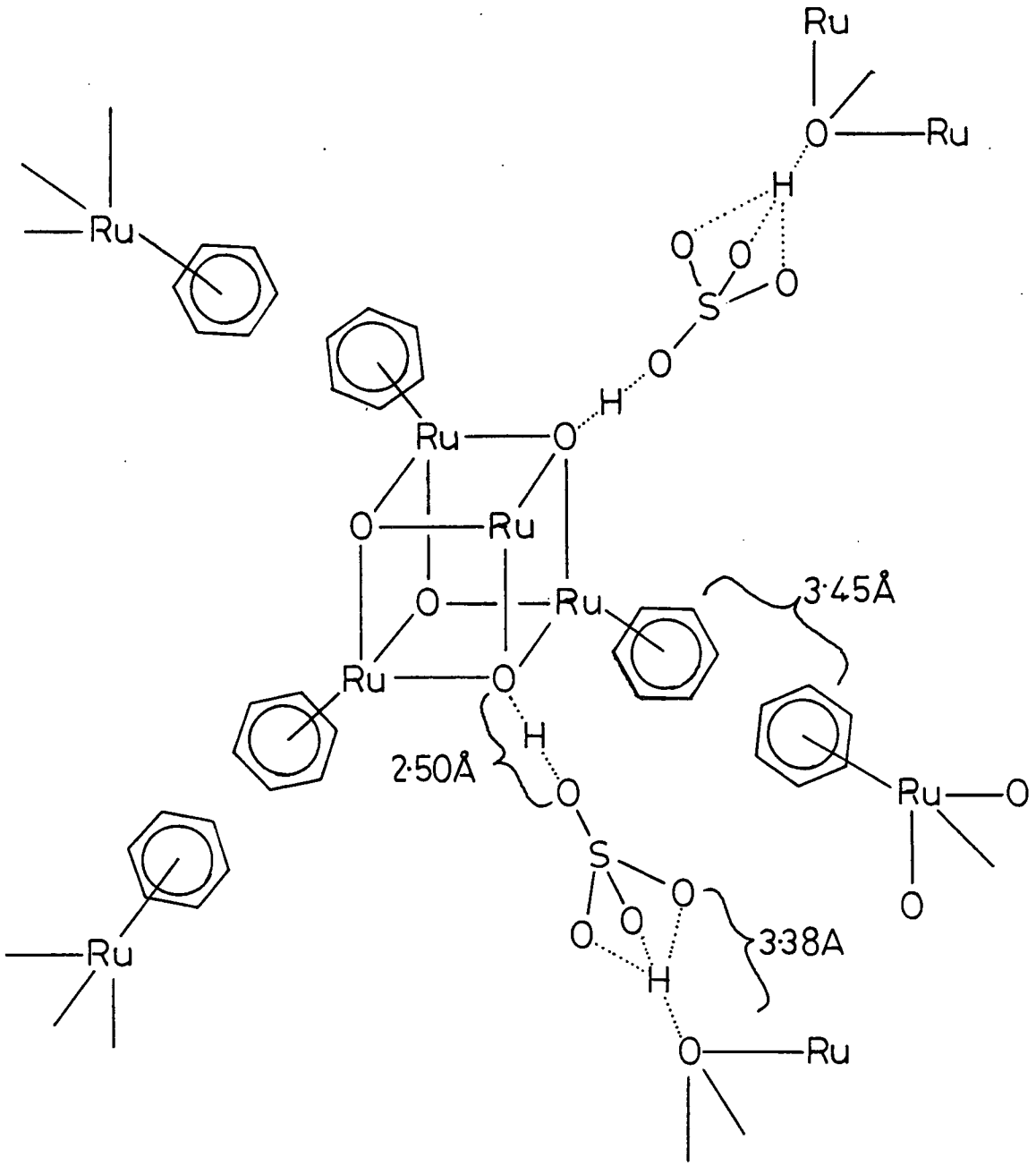
Figure 2.5 The molecular structure of the cation $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$



The crystal structure determination gives an indication as to why both arenes other than benzene, and bridging ligands other than hydroxyl do not form similar complexes. Each of the cations $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$ can be regarded as being bonded to eight others through the cube corners. At the vertices occupied by Ru, this is achieved by strong Van der Waals interactions between the benzene rings of adjacent cations. These lie in parallel planes separated by 3.45 Å (cf. 3.35 Å in graphite). This close approach implies that the rings are staggered with respect to one another (C...C = 3.53 Å) but such local ordering will have no effect on the relative positions of pairs of benzene rings elsewhere in the structure. At the same time, the vertices of the cube occupied by OH are hydrogen bonded to the sulphate ion lying between them. In whichever way it is orientated, an atom O(2) will be 2.50 Å from the oxygen at the corner of the cube, while the three atoms of type O(3) will be 3.38 Å from the O(1) oxygen of another cube. The nature of these interactions are illustrated in Figure 2.6. Thus the stability of the crystal, and probably of the cation, depends both on the arenes having no aliphatic substitutents and the anions being of a suitable size to bridge a gap between two OH groups for which O...O is 7.67 Å and H...H 5.50 Å.

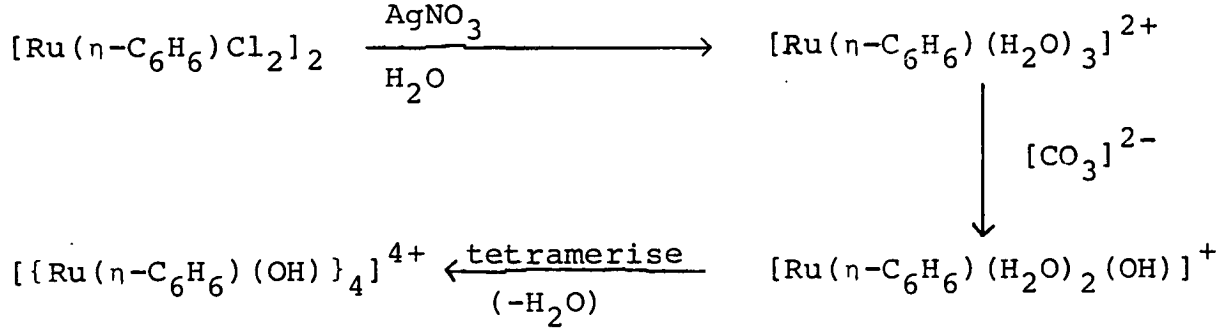
A possible mechanism of formation of the tetranuclear cation is *via* deprotonation of the trisaqua cation $[Ru(\eta\text{-}C_6H_6)(H_2O)_3]^{2+}$, (generated *in situ* in high yield by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with aqueous $AgNO_3$ [96])

Figure 2.6 A schematic representation of the interactions present in the crystal structure of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$



by equimolar amounts of $[CO_3]^{2-}$ to give the $[Ru(\eta\text{-}C_6H_6)(H_2O)_2(OH)]^+$ cation. The combination of the bridging propensity of hydroxo groups and the desire of ruthenium(II) to exhibit six coordination[97] could then lead to tetramerisation of the $[Ru(\eta\text{-}C_6H_6)(H_2O)_2(OH)]^+$ cation with concomitant elimination of water to form the $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$ cubane cluster cation (see Scheme 2.6). This process is enhanced by the presence of excess sulphate ion which removes the tetrameric cation from solution. In fact, if an aqueous solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ is treated with an equimolar amount of Na_2CO_3 before addition of Na_2SO_4, then only the previously discussed cations $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)]^+$ and $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ are observed.

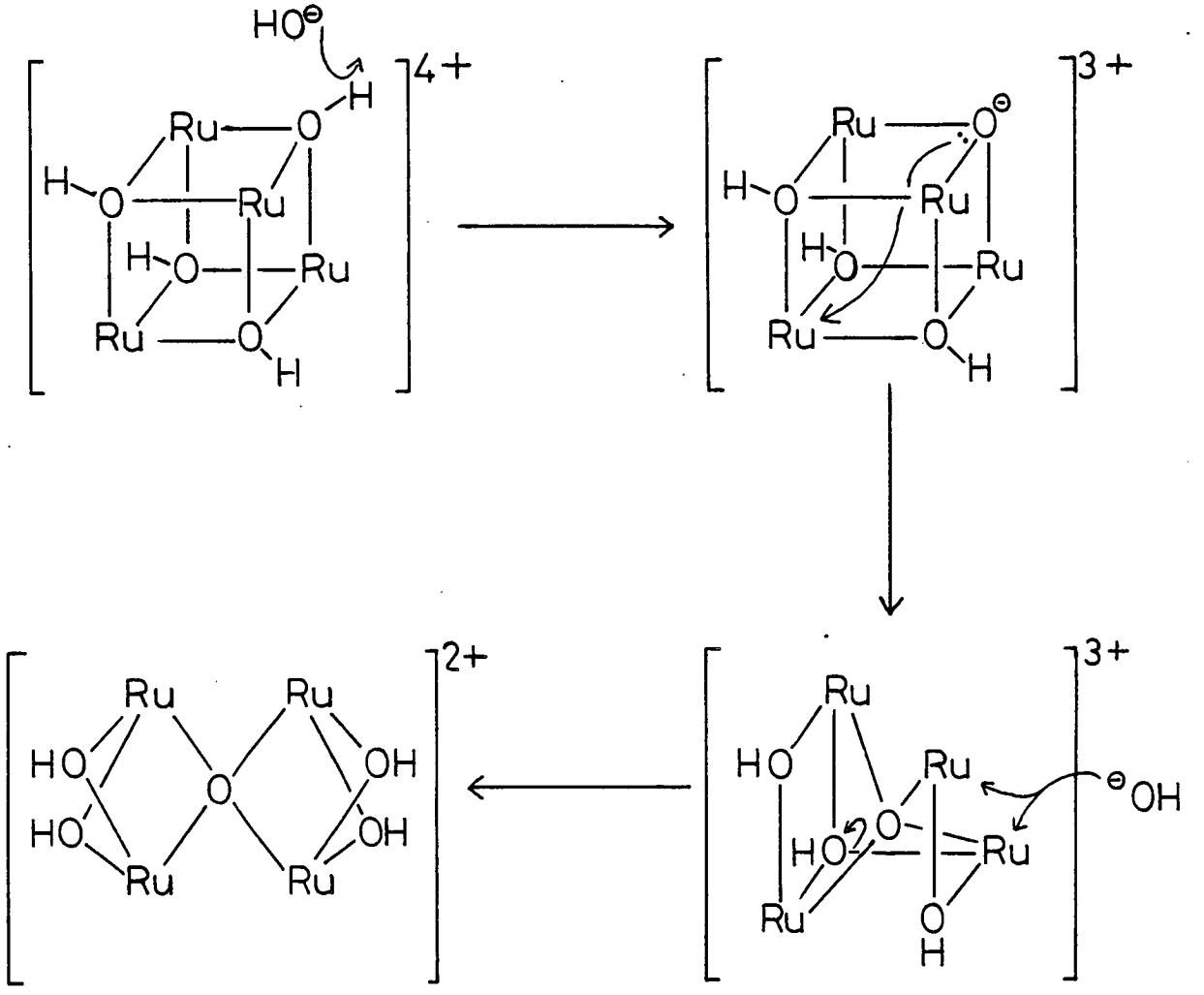
Scheme 2.6 A mechanism for the formation of the cation $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$



In support of this observation, treatment of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$ with an excess of either aqueous Na_2CO_3 or NaOH followed by addition of $Na[BPh_4]$ readily gives $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2H_2O$. The ^1H n.m.r. spectrum in $(CD_3)_2CO$ at 298 K showed only one $\eta\text{-}C_6H_6$ resonance at δ5.60 ppm which indicated that no $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ (δ5.33 ppm (^1H n.m.r.)) had been formed by this route. The mechanism of formation of this complex may involve initial deprotonation of one of the hydroxyl groups at a corner of the "cube", followed by coordination of the oxygen atom to the ruthenium atom to which it is not already bound. Subsequent attack by $[OH]^-$ gives rise to the previously described product (see Scheme 2.7).

Although $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ does not react with LiBr in the absence of acid, $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$ reacts with aqueous LiBr (1:2 molar ratio) to give an orange solution from which orange-yellow solids could be precipitated by addition of either $NH_4[PF_6]$ or $Na[BPh_4]$. These compounds analysed quite closely for "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_2Br]Y$" (Y = PF_6, BPh_4) but their ^1H n.m.r. spectra in CD_3NO_2 contained several $\eta\text{-}C_6H_6$ resonances. A possible explanation of this observation is that in solution the $-(\mu\text{-}OH)_2(\mu\text{-}Br)-$ cation rapidly rearranges to give a mixture containing the $-(\mu\text{-}OH)_3-$, $-(\mu\text{-}OH)_2(\mu\text{-}Br)-$, $-(\mu\text{-}OH)(\mu\text{-}Br)_2-$ and $-(\mu\text{-}Br)_3-$ cations, (cf. related studies on mixed halo-bridged binuclear cations[9]). The same species are obtained on

Scheme 2.7 A mechanism for the formation of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ from $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4]^{4+}$, (benzene groups omitted for clarity



mixing nitromethane solutions of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3]^+$ cations. On leaving in solution the "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_2Br]^+$" cation slowly deposits some insoluble $[Ru(\eta\text{-}C_6H_6)Br_2]_2$ and this is the only product obtained when the tetramer is treated with an excess of LiBr.

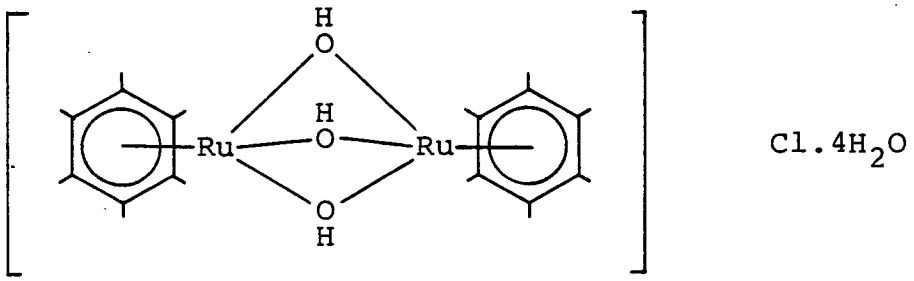
Unlike the $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$ cation, this tetrameric species is susceptible to attack by Lewis bases. With pyridine or 4-methylpyridine (L) a di-cationic product $[\{Ru(\eta\text{-}C_6H_6)(OH)L\}_2][PF_6]_2$, can be isolated when $NH_4[PF_6]$ is added to the reaction mixture. However, reaction of the complex with an excess of 1,10-phenanthroline results in the displacement of the π-bonded benzene, and addition of $NH_4[PF_6]$ precipitates the well-known $[Ru(phen)_3][PF_6]_2$ [13].

2.4 The synthesis of some new triple bridged binuclear η-arene ruthenium(II) and osmium(II) complexes

General methods for the synthesis of triple hydroxo and alkoxo bridged η-arene ruthenium(II) complexes have already been outlined in the introduction to this chapter. The range of compounds available has now been extended and a new synthetic route to the alkoxo bridged compounds developed.

The reaction of $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ with an excess of NaOH in water gives a pale green precipitate. The infrared spectrum of this complex contained a

characteristic ν(OH) stretching band at 3420 cm^{-1}. No bands attributable to ν(Ru-Cl) are observed but a band at 500 cm^{-1} can be tentatively assigned to a ν(Ru-O) vibration. The ^1H n.m.r. spectrum in CD_3NO_2, of the $[BPh_4]^-$ salt, consists of $[BPh_4]^-$ multiplets and a strong singlet at δ2.05 ppm, assigned to the methyl groups of the arene ring, but no signal is observed for the hydroxyl proton. Integration of the two signals is in the ratio of ca. 20:36. With this particular arene no evidence is found for any double bridged complexes analogous to (30) or (35) and the product is assigned a triple bridged structure (37) (c.f. $[Ru_2(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2(OH)_3]Cl.3H_2O$ - Section 2.2). Microanalyses fit well for the formulation $[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Cl.4H_2O$ and a molar conductivity, in nitromethane, of Λ_m = 50 S cm^2 mol^{-1}, for a 5 x 10^{-4} mol dm^{-3} solution, is consistent with the presence of a 1:1 electrolyte. Unfortunately the complex was too insoluble for conductivity measurements to be made over a meaningful concentration range.

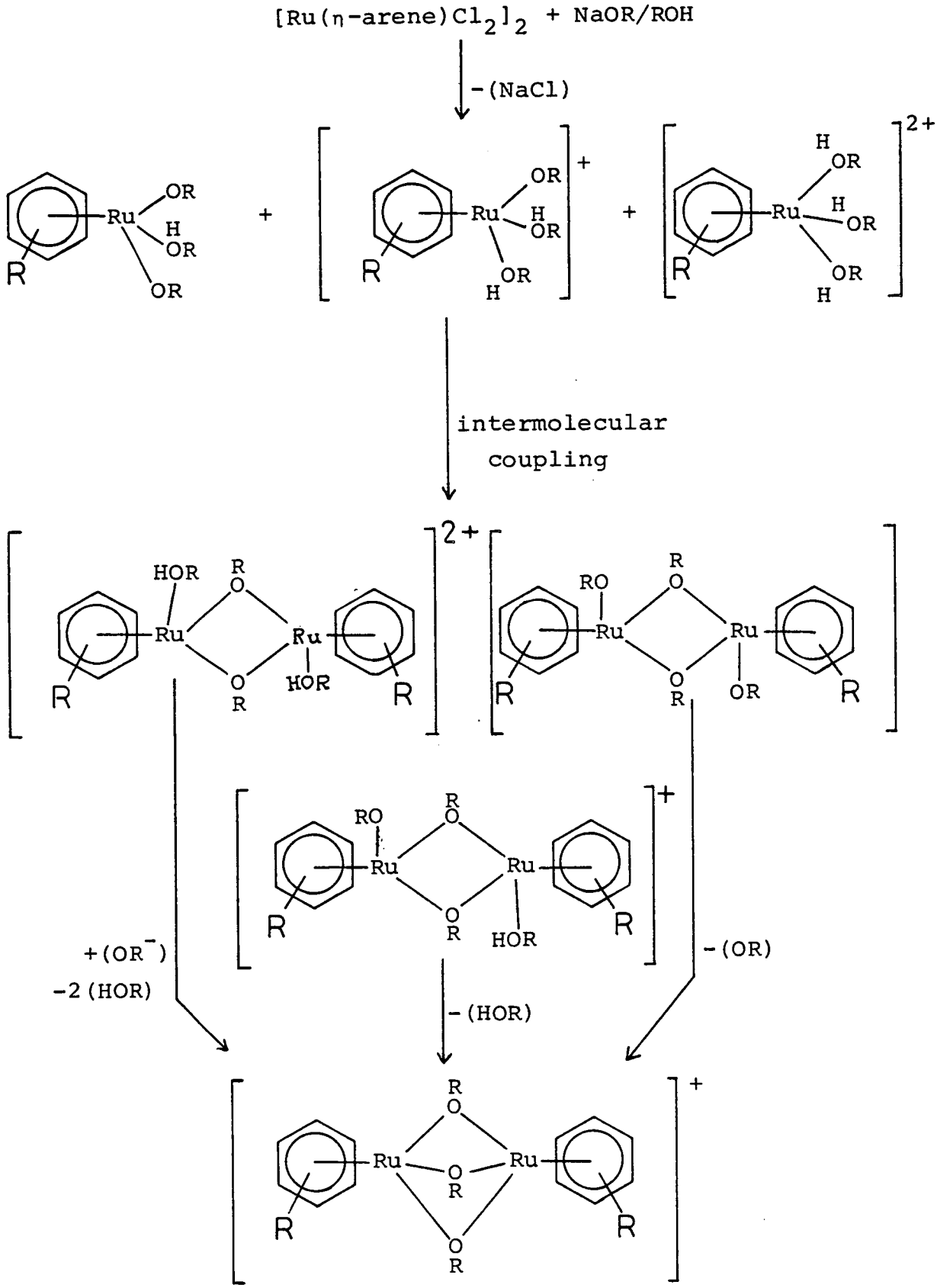


(37)

This result reaffirms the observation made previously that the greater the degree of substitution of the arene ring, the greater the tendency to form the triple hydroxo bridged complex since no evidence for the formation of double hydroxo bridged intermediates analogous to (30) has been found for arene = p-cymene, mesitylene or hexamethylbenzene.

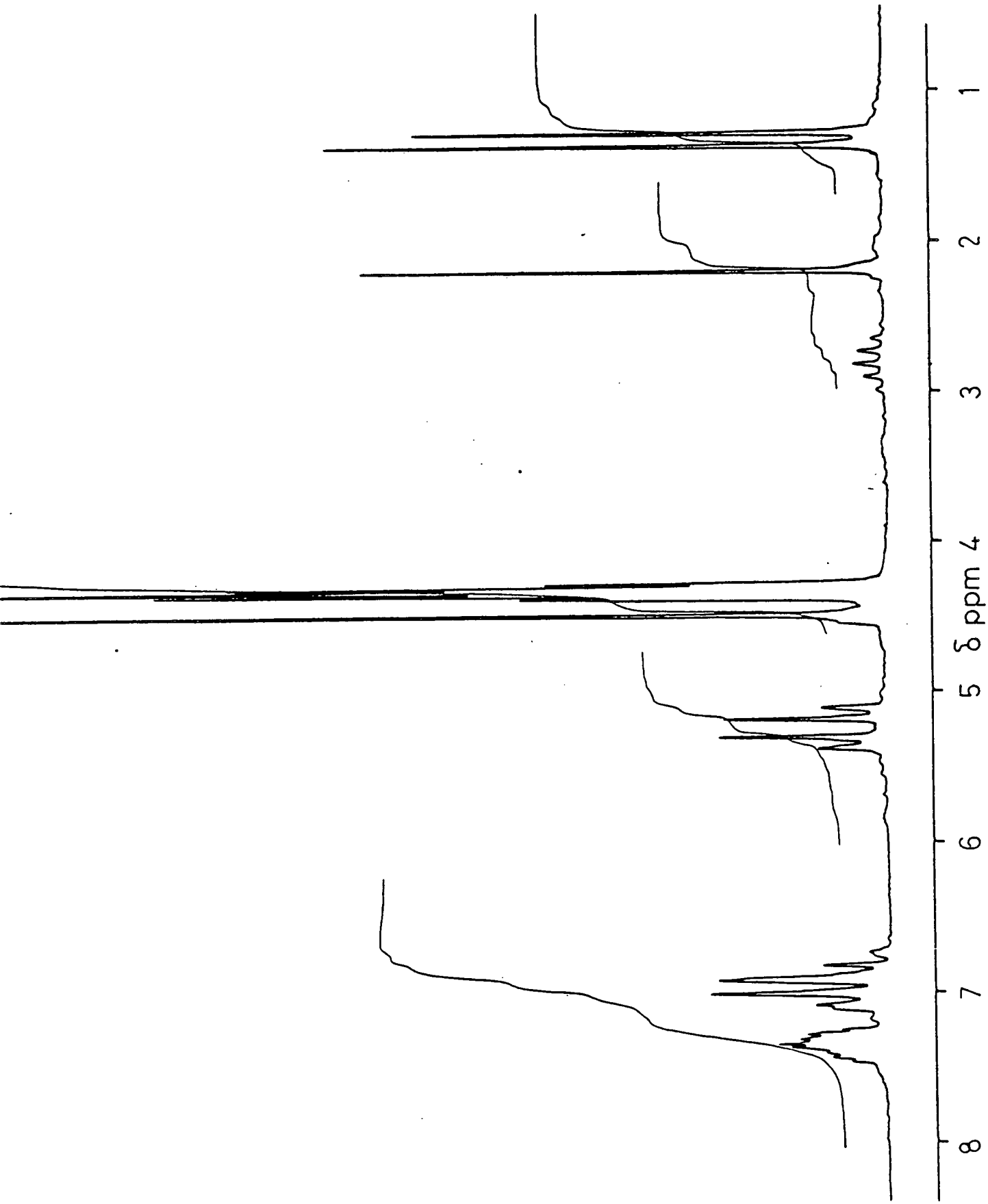
The complexes $[Ru_2(\eta\text{-}C_6Me_6)_2(OMe)_3][BPh_4]$ and $[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ were prepared by reaction of the appropriate dimer $[M(\eta\text{-arene})Cl_2]_2$ with a freshly prepared solution of NaOMe in MeOH. In both cases the reaction proceeds smoothly and addition of $Na[BPh_4]$ to the reaction mixtures gives the products as microcrystalline yellow and grey solids respectively. The formulation of the products as the triple methoxo bridged complexes was supported by ^1H n.m.r. and infra-red spectra, elemental analyses and conductivity measurements, in nitromethane. A possible mechanism for the formation of these species from $[M(\eta\text{-arene})Cl_2]_2$ is shown in Scheme 2.8. The first step in this process involves displacement of the chloride ligands by a mixture of methoxo and methanol ligands. The monomeric species generated may then couple to form a variety of binuclear complexes, followed by loss of one or more methanol ligands and subsequent attack by methoxide to give the stable tri-μ-methoxo cation.

Scheme 2.8 A possible mechanism for the formation of triple alkoxo bridged complexes by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ with NaOR/ROH



Previously it had been found that reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = $1,4\text{-MeC}_6H_4CHMe_2$, $1,3,5\text{-}C_6H_3Me_3$) with NaOR/ROH (R = Me, Et) did not give the pure triple bridged product, but a mixture of two or more complexes[84]. This result was attributed to the indiscriminate way in which the $[BPh_4]^-$ anion removes all the cationic species present from solution, i.e. some of the species present in the mixture may be the intermediates postulated in the reaction mechanism, shown in Scheme 2.8. Similar mixtures were also obtained upon refluxing $[Ru_2(\eta\text{-arene})_2(OH)_3][BPh_4]$ (arene = $1,4\text{-MeC}_6H_4CHMe_2$; $1,3,5\text{-}C_6H_3Me_3$) in ROH (R = Me, Et). A synthetic route has now been developed which gives pure samples of $[Ru_2(\eta\text{-}1,4\text{-MeC}_6H_4CHMe_2)_2(OR)_3][BPh_4]$ (R = Me, Et). Thus, if $[Ru(\eta\text{-}1,4\text{-MeC}_6H_4CHMe_2)Cl_2]_2$ is shaken in CH_3CN containing "80-90% $NaNH_2$", a dark yellow-brown solution is obtained. After filtering through celite to remove NaCl and excess "$NaNH_2$", the solvent is evaporated off and the residual oil treated with a methanol solution of $Na[BPh_4]$. On standing, a yellow crystalline solid is deposited. The infrared spectrum of this product contains a strong ν(C-O) vibration at ca. 1050 cm^{-1} and no bands attributable to ν(Ru-Cl). The ^1H n.m.r. spectrum in CD_3NO_2 (see Figure 2.7) reveals the usual $[BPh_4]^-$ multiplets between δ6.8 and 7.5 ppm, an AB pattern, at δ5.24 ppm, a septet, at δ2.82 ppm, a singlet at δ2.20 ppm and a doublet at δ1.32 ppm (all from the η-p-cymene ring) and a sharp singlet at 4.49 ppm due to the -OMe groups. Integration of this

Figure 2.7 The ^{1}H n.m.r. spectrum in CD_3NO_2 of $[Ru_2(n\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OMe)_3][BPh_4]$



^1H n.m.r. spectrum which shows the ratio $[BPh_4]^-$: $MeC_6H_4CHMe_2$:$[OMe]^-$ is 1:2:3 and the analysis figures (see Table 2.1), indicate the triple methoxo bridged formulation $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OMe)_3][BPh_4]$. Further support for this formulation comes from conductivity measurements since in nitromethane a molar conductivity of Λ_m = 56 S cm^2 mol^{-1} (for a 10^{-3} mol dm^{-3} solution), is obtained and a plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ gives a straight line of slope 136 which is consistent with that expected for a 1:1 electrolyte.

If the oil remaining after the removal of the solvent is treated instead with an ethanolic solution of $Na[BPh_4]$, then the orange crystals deposited have a ^1H n.m.r. spectrum in CD_3NO_2 which consists of the usual resonances due to $[BPh_4]^-$ and η-1,4-$MeC_6H_4CHMe_2$ and additionally a triplet, at δ1.50 ppm, and quartet, at δ4.62 ppm, attributed to -OEt groups. Integration of these signals shows that the ratio of $[BPh_4]^-$: $MeC_6H_4CHMe_2$:$[OEt]^-$ is 1:2:3. This complex can thus be formulated as $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OEt)_3][BPh_4]$ and a partial X-ray structural analysis has confirmed the triple bridged binuclear nature of this complex. Unfortunately a full refinement of the structure was not possible due to extensive rotational disorder but the Ru-Ru, 3.04 Å, Ru-O, 2.03 Å, and Ru-C, 2.20 Å distances were of the predicted magnitude for a complex of this geometry. The compounds $[Ru_2(\eta\text{-}C_6H_6)_2(OR)_3][BPh_4]$ (R = Me, Et) have also been prepared by this new synthetic route (See Experimental section).

Attempts to synthesise longer chain alkoxides such as ^{i}PrO- or ^{n}BuO- using either the $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO/ROH$ or $[Ru(\eta\text{-}C_6H_6)Cl_2]_2/NaOR$ routes were unsuccessful since extensive decomposition occurred and no arene ruthenium complexes could be isolated from the reaction mixture. Treatment of $[Ru(\eta\text{-arene})(CH_3CN)_3]^{2+}$ cations (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$), generated *in situ* from $[Ru(\eta\text{-arene})Cl_2]_2/NaNH_2/CH_3CN$, with iso-propanol or isobutanol solutions of $Na[BPh_4]$ did not, however, result in decomposition, but in the formation of yellow air stable solutions. Unfortunately, extreme difficulty was experienced in isolating any solid product from the reaction mixture, no doubt due to the high solubility of the alkoxo species generated. However, in the case of the benzene complexes an alternative route to these compounds is now available.

The reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ with isobutanol under mild conditions (40°C, 10-15 minutes) produces a microcrystalline yellow precipitate. The infrared spectrum of this product has lost all the bands previously attributed to the aqua and hydroxyl ligands but an intense band at 1050 cm^{-1} is assigned to a ν(C-O) vibration. The ^{1}H n.m.r. spectrum in CD_3NO_2 shows a singlet at δ5.36 ppm due to the benzene ring, two doublets at δ1.12 and 4.27 ppm (in the ratio 3:1) and a multiplet at δ2.28 ppm, attributed to the iso-butoxide ligand, as well as the normal $[BPh_4]^-$ resonances between δ6.8 and 7.5 ppm. Integration of the signals showed the ratio of C_6H_6:i-BuO;$[BPh_4]^-$ is 2:3:1. The compound

behaved as a 1:1 electrolyte in CH_3NO_2 solution and hence this evidence suggests that its structure is a binuclear triple bridged one similar to that of the other areneruthenium(II) alkoxides.

The reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ with iso-propanol proceeds in a similar manner to that described above. The yellow microcrystalline solid obtained has a very similar infrared spectrum to that of the butoxide compound. Its ^1H n.m.r. spectrum in CD_3NO_2 consists of the usual $[BPh_4]^-$ resonances, a singlet at δ5.46 ppm due to the arene ligand and a doublet and septet, at δ1.48 and 4.89 ppm respectively, ascribed to the iso-propoxide ligands. Integration of the ^1H n.m.r. spectrum is consistent with a ratio of C_6H_6:i-PrO$^-$:$[BPh_4]^-$ of 2:3:1. The $^{13}C\text{-}\{^1H\}$ spectrum in CD_3NO_2 consists of three lines, (in addition to the $[BPh_4]^-$ signals at δ120-140 ppm), at δ78.80, 33.82 and 19.74 ppm. The resonance at δ78.80 ppm is readily assigned to η-benzene, while a proton coupled spectrum indicates that the signal at δ33.82 ppm arises from $-O\underline{C}H(CH_3)_2$ and the signal at δ19.74 ppm from $-OCH(\underline{C}H_3)_2$. The formulation of the product as $[Ru_2(\eta\text{-}C_6H_6)_2(i\text{-}PrO)_3][BPh_4]$ fits well with the analytical data (see Table 2.1) and conductivity measurements in CH_3NO_2 confirm the presence of a 1:1 electrolyte (Λ_m = 52 S cm^2 mol^{-1}, for a 10^{-3} mol dm^{-3} solution). Unfortunately it has not been possible to extend these reactions to other arenes

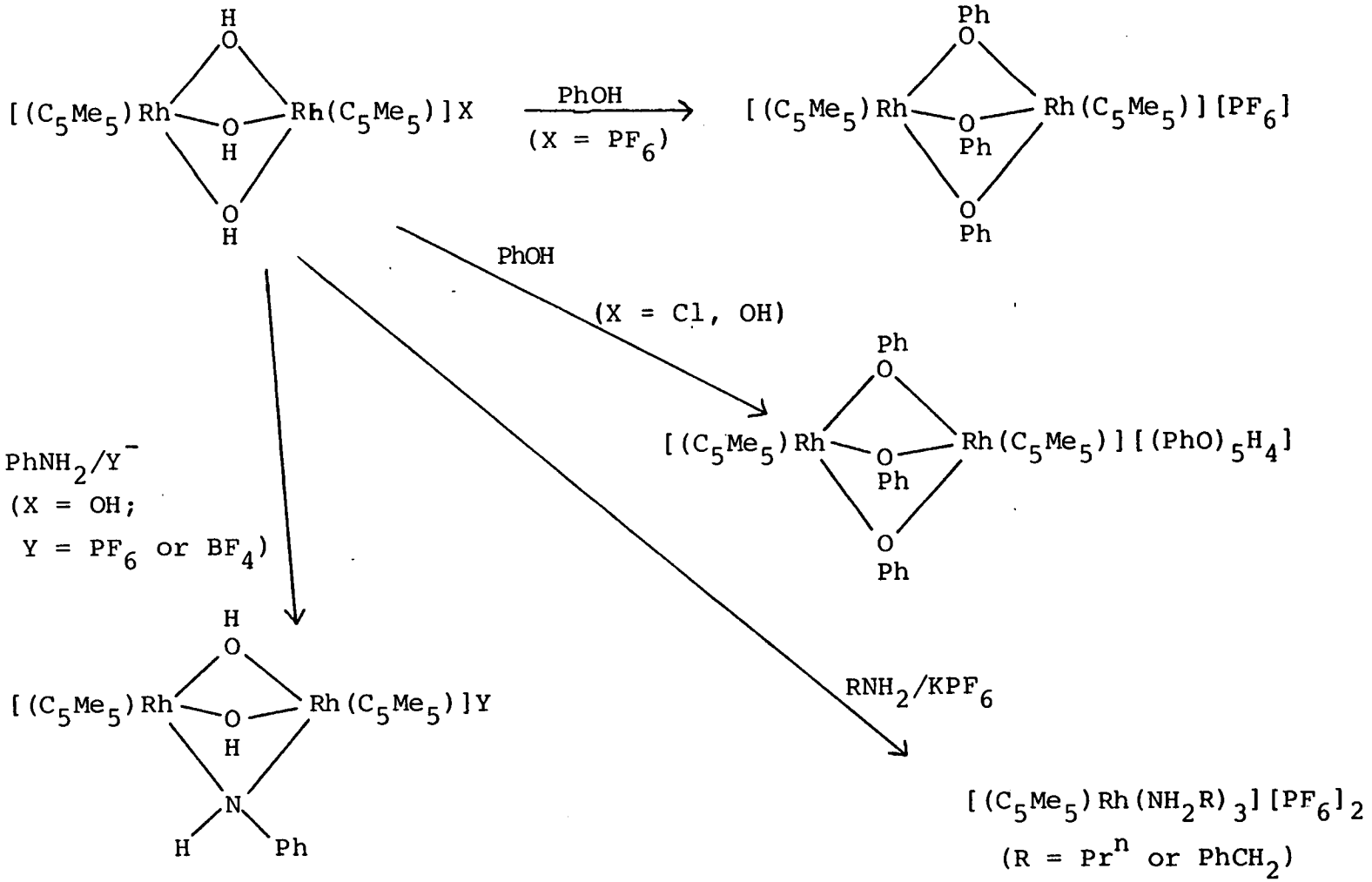
as a suitable starting material is not available. In addition, if these reactions are carried out at higher temperatures or over a greater period of time (>30 minutes), then extensive decomposition occurs and the products described above cannot be isolated. This decomposition probably occurs *via* ruthenium hydride intermediates, generated by facile β-elimination steps from the alkoxo species. Good evidence for hydride formation comes from the reported isolation of a variety of bridged hexamethylbenzene and mesitylene ruthenium(II) hydrido complexes, obtained by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ [90], $Ru(\eta\text{-arene})Cl(O_2CR)$ and $Ru(\eta\text{-arene})(O_2CR)_2$ [30] with aqueous solutions of iso-propoxide ions. Similar hydrido complexes may be formed in the reactions between benzene complexes and longer chain alkoxides, under anything other than very mild conditions, but due to the comparative weakness of the ruthenium-benzene bonds, loss of benzene and subsequent product decomposition results.

Although the tri-μ-alkoxo dirhodium (and iridium) complexes $[M_2(\eta\text{-}C_5Me_5)_2(OR)_3]X$ have never been prepared the tri-μ-phenoxo complex has recently been synthesised by reaction of $[M_2(\eta\text{-}C_5Me_5)_2(OH)_3]X$ (X = PF_6, Cl, OH) with aqueous phenol (Scheme 2.9). The stability of this complex was attributed to the fact that there were no hydrogens that could be readily lost to the metal [98].

The reaction of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ with phenol under similar conditions did not give the analogous tri-μ-phenoxo compound. However the complex $[Ru_2(\eta\text{-}C_6H_6)_2(OPh)_3][BPh_4]$ has been successfully prepared by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with Na[OPh] in methanol. Addition of $Na[BPh_4]$ to the yellow solution obtained on warming $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ in a mixture of MeOH/PhOH/Na[OPh] gave a precipitate whose infrared spectrum did not contain any bands attributable to ν(O-H) vibrations but did contain a strong ν(C-O) band at 1065 cm^{-1}. In addition, a band at 490 cm^{-1} is tentatively assigned to the ν(Ru-O) stretching vibration. The ^1H n.m.r. spectrum in CD_3NO_2 contains a singlet at δ5.12 ppm due to the π-bonded benzene and a complex multiplet, centred at δ6.95 ppm, due to the overlapping signals of the $[BPh_4]^-$ anion and the μ-phenoxo groups. The formulation of the product as $[Ru_2(\eta\text{-}C_6H_6)_2(OPh)_3][BPh_4]$ is in good agreement with the analytical and conductivity data (see Table 2.1).

The reaction of $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3][OH]$ with aniline has recently been reported to give the new complex $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_2(NHPh)][X]$ (X = PF_6, BF_4)[99], in which only one of the hydroxyl bridging ligands has been replaced (see Scheme 2.9). In contrast, reaction of $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3][OH]$ with n-propylamine or benzylamine gives monomeric products of the type $[Rh(\eta\text{-}C_5Me_5)(NH_2R)_3][PF_6]_2$. The difference in binding

Scheme 2.9 The reactions of $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]X$ with phenol and amines



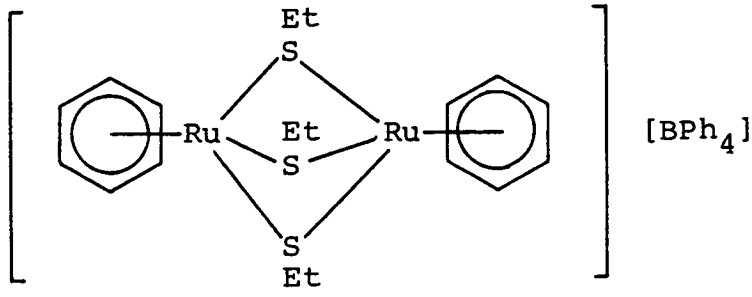
of the aliphatic and aromatic amines was attributed to the relative basicities and acidities of the different types of primary amines.

Attempts to prepare isoelectronic areneruthenium(II) complexes, either by reaction of the hydroxo complexes with these amines or by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) with the sodium salts of the amines were unsuccessful, in all cases. The explanation for this may lie in the presence of a facile route to decomposition, via β-hydride-elimination, or may be due to the presence of strong steric interactions between the amines and/or the arene ring, analogous to those reported for the rhodium complexes.

The reactions of a variety of arene ruthenium(II) complexes with ethanethiol and its salts have also been examined in an attempt to isolate some new triply bridged diruthenium(II) complexes. The related complexes $[Ru_2(PMe_2Ph)_6(SEt)_3]X$ (X = PF_6, BPh_4) have been prepared[100] by treatment of the red solution, (obtained on refluxing $[RuH(cod)(NH_2NMe_2)_3]X$ with a three fold excess of PMe_2Ph in acetone), with EtSH. Obviously this route was not available for the arene complexes and initial investigations therefore followed a parallel route to the synthesis of the alkoxides. Unfortunately, $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ proved to be totally insoluble, even in refluxing EtSH and only the starting materials were recovered on work up.

The reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, $1,4\text{-}MeC_6H_4CHMe_2$, C_6Me_6) with a "fresh prepared" solution of NaSEt in EtSH resulted in the rapid decomposition of the starting material. A successful synthesis has however been developed, using $Pb(SEt)_2$ as the source of the thiol. Treatment of a CH_3CN solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with an excess of $Pb(SEt)_2$ results in the formation of a dark brown solution. After filtering through celite to remove $PbCl_2$ and any unreacted $Pb(SEt)_2$, the solvent is removed and the residue treated with a methanol solution of $Na[BPh_4]$. The infrared spectrum of the resultant yellow precipitate contained no bands attributable to ν(Ru-Cl) vibrations. Bands at 605, 809 and 840 cm^{-1} are characteristic of π-bonded benzene, a weak band at 610 cm^{-1} may be due to ν(S-C) vibrations and a broad band at 365 cm^{-1} is tentatively assigned to ν(Ru-S) vibrations. In addition, the characteristic bands, between 680-750 cm^{-1} and 1300-1500 cm^{-1}, due to $[BPh_4]^-$ are observed. The ^1H n.m.r. spectrum in CD_3NO_2 contains a singlet at δ5.69 ppm due to the π-bonded benzene and a triplet and quartet, at δ1.30 and 2.35 ppm respectively, due to the $[SEt]^-$ groups, as well as the usual $[BPh_4]^-$ resonances. Integration of the ^1H n.m.r. spectrum suggests the formulation $[Ru_2(\eta\text{-}C_6H_6)_2(SEt)_3]$-$[BPh_4]$ (38). The $^{13}C\text{-}\{^1H\}$ spectrum contains three lines in addition to the usual signals from $[BPh_4]^-$. The signal at δ84.47 ppm is due to the π-bonded benzene,

while the other two signals, at δ32.76 (CH_2) and 17.04 ppm (CH_3), are assigned to the thiol ligands.

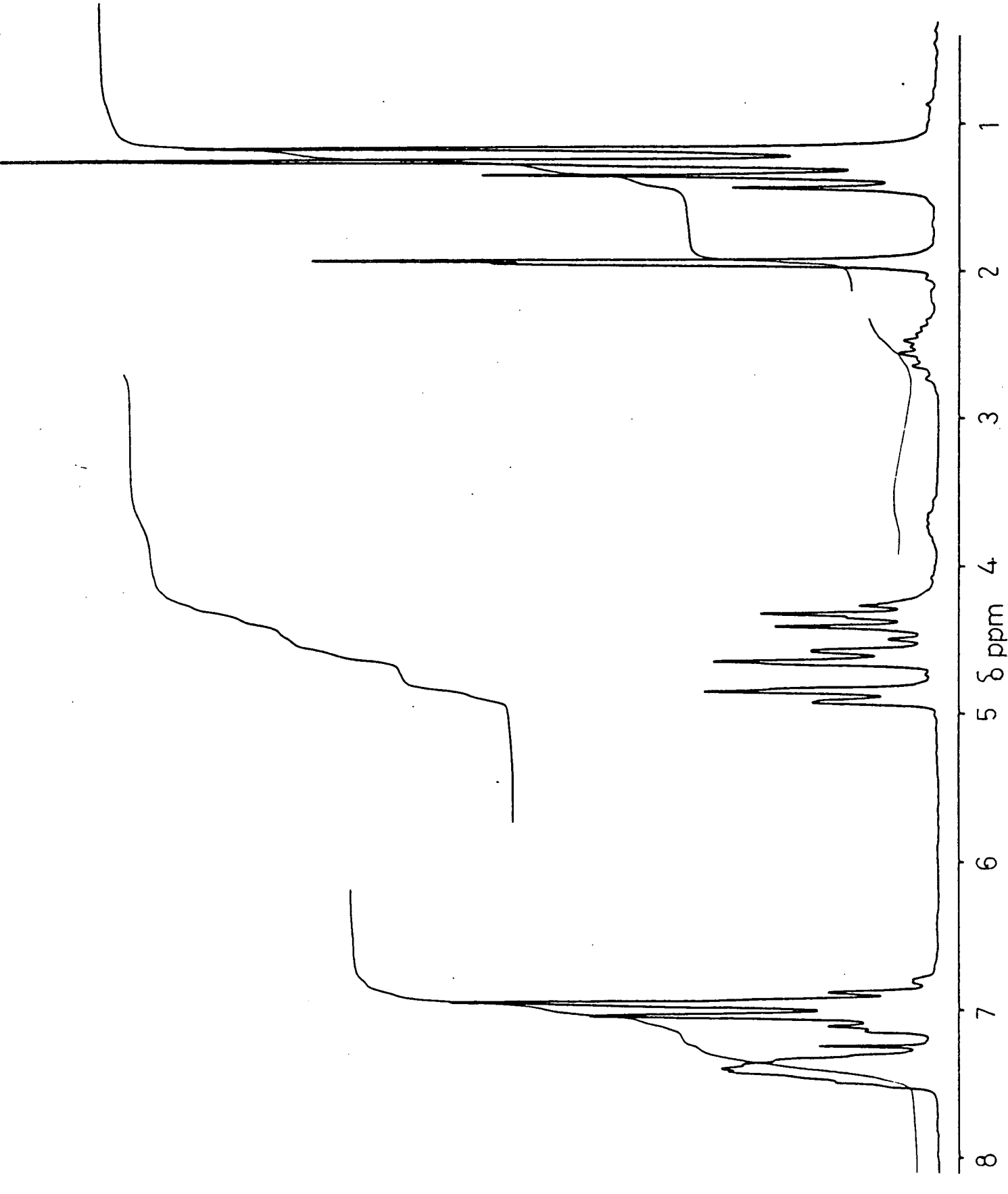


(38)

Analysis fits well for this formulation (see Table 2.1) and a conductivity measurement in nitromethane is consistent with a 1:1 electrolyte (Λ_m = 48 S cm^2 mol^{-1} at a concentration of 10^{-3} mol dm^{-3}).

The η-p-cymene complex is prepared in a similar manner, although longer reaction times are required for generation of pure products. The infrared spectrum of the product is very similar to that described for the benzene complex. The ^1H n.m.r. spectrum in $CDCl_3$ (see Figure 2.8) contains the usual $[BPh_4]^-$ resonances, characteristic resonances due to the η-p-cymene ring (δ4.74 (AB); δ2.50 (sp); 1.93 (s); δ1.21 (d) ppm) and a quartet, at δ4.37 ppm, and a triplet, partially overlapping with the doublet of the isopropyl group, at δ1.43 ppm. The integration of the ^1H n.m.r. spectrum is consistent with the formulation of the product as $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$. Analysis fits well for this formulation and further support for this comes from conductivity measurements. In nitromethane,

Figure 2.8 The ^{1}H n.m.r. spectrum in $CDCl_3$ at 298 K of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$



a molar conductivity Λ_m = 48 S cm^2 mol^{-1}, for a 10^{-3} mol dm^{-3} solution is obtained and a plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ gives a straight line of slope 115 which is consistent with the presence of a 1:1 electrolyte.

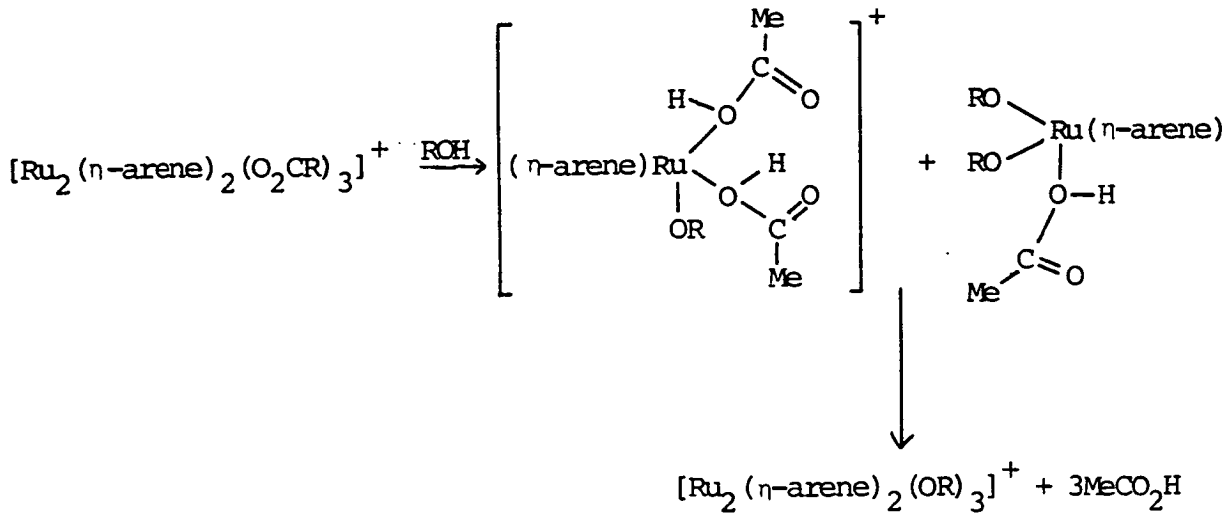
Finally, attempts to synthesise methylene bridged arene ruthenium(II) complexes by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) with diethyl ether solutions of LiMe proved unsuccessful as, even under mild conditions, only extensive decomposition was observed.

2.5 The reactions of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$) with NaO_2CR/HO_2CR (R = CH_3, CF_3)

The preparation of the tri-μ-carboxylato complex $[Ru_2(\eta\text{-}C_6Me_6)_2(O_2CMe)_3][PF_6]$ by reaction of $Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2.H_2O$ with aqueous $Ag[PF_6]$ has already been reported[60]. It was hoped that it would be possible to synthesise a wider range of these areneruthenium(II) complexes by reaction of $[Ru(\eta\text{-arene})Cl_2]_2$ with "freshly prepared" NaO_2CMe in HO_2CMe in a manner analogous to the synthesis of the tri-μ-alkoxo complexes.

The reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]$ with NaO_2CR/HO_2CR produces a yellow solution. Removal of the solvent and subsequent treatment of the residual oil with a methanolic solution of $Na[BPh_4]$ gives a microcrystalline yellow solid. The infrared spectrum of this product

did not however contain any bands characteristic of either bidentate or unidentate carboxylate groups. A strong band at ca. 1050 cm^{-1} was assigned to the ν(C-O) vibrations of a bridging alkoxo ligand. The ^1H n.m.r. spectrum in CD_3NO_2 did not have any signals in the region δ1.5 - 2.5 ppm (the characteristic region for acetate) but was totally consistent with the formation of the well-known $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$. If an ethanolic solution of $Na[BPh_4]$ was used in the preparation then the product isolated was characterised as the well known $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$[68]. The reactions with $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ are similar in that no carboxylato complexes are isolated but the products tended to be a mixture of alkoxo species similar to that previously described[84]. A possible explanation for these observations may be that the carboxylato ligand is extremely labile under these conditions and although a cation $[Ru_2(\eta\text{-arene})_2(O_2CMe)_3]^+$ may be formed in solution, this is readily protonated by alcohol, bridge cleavage may then occur and the mixed carboxalato-alkoxo monomers recombine with loss of carboxylic acid to form the stable tri-μ-alkoxo complexes (Equation [8]).



$[Ru_2(\eta\text{-arene})_2(O_2CR)_3]^+ \xrightarrow{ROH} [(\eta\text{-arene})Ru(OR)(\mu\text{-H})(\mu\text{-}O_2CMe)]^+ + Ru(\eta\text{-arene})(RO)_2(\mu\text{-OH})(\mu\text{-}O_2CMe)$

$[Ru_2(\eta\text{-arene})_2(OR)_3]^+ + 3MeCO_2H$

.....[8]

In support of this explanation, it should be noted that it has already been shown that the monomeric complexes $Ru(\eta\text{-arene})Cl(O_2CR)$ and $Ru(\eta\text{-arene})(O_2CR)_2$ react with NaOR/ROH to give the well known tri-μ-alkoxo complexes. Also, unlike many other ligands, (tertiary phosphines, bipyridyl, dithioacids etc.), the carboxylate ligand is incapable of displacing the arene ring, even upon refluxing, $[Ru(\eta\text{-}C_6H_6)_2Cl_2]_2$ with RCO_2H, for extended periods where the only product obtained is $Ru(\eta\text{-}C_6H_6)Cl(O_2CR)$ (see Chapter 1).

The reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with NaO_2CCF_3/HO_2CCF_3 and then $Na[BPh_4]$/MeOH gave an orange product whose infra-red spectrum contained weak bands attributed to $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ stretches at 1630 and 1450 cm^{-1} respectively. However both the ^1H and ^{19}F n.m.r. spectra in CD_3NO_2 indicated that the product was not a single compound.

The reaction of $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ under similar conditions gave a product whose infrared spectrum also contained bands attributable to $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ vibrations at 1640 and 1470 cm^{-1} respectively. The spectrum also contained a broad band at 270 cm^{-1} attributed to ν(Ru-Cl) bridging vibrations. The only solvent in which the complex was sufficiently soluble for its n.m.r. spectrum to be recorded was CD_3NO_2 but unfortunately dissolution in this medium led to rapid decomposition. Thus although the ^{19}F n.m.r. spectrum showed four resonances, it is not clear whether these were all due to the initial complex or to its decomposition products. Elemental analysis (C, H, Cl, F) are consistent with the formulation "$[Ru_4(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_4Cl_5(O_2CCF_3)][BPh_4]_2$". However, recrystallisation of the complex from CH_2Cl_2/Et_2O gave orange crystals, the infrared spectrum of which no longer contained any bands attributable to $\nu(OCO)_{asym}$ or $\nu(OCO)_{sym}$ vibrations, but the ν(Ru-Cl) stretch at 270 cm^{-1} is retained. No ^{19}F n.m.r. signal was now observed and the ^1H n.m.r. spectrum consisted solely of bands attributable to η-p-cymene. This material was identified as $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4]$ by comparison with a genuine sample of this complex prepared by an alternative route. Full confirmation of the identity of this recrystallised product was provided by an X-ray structural analysis (see below).

It would appear likely that the product obtained initially, rather than being the tetranuclear complex suggested, is a mixture of binuclear complexes containing the bridging units $-RuCl_3Ru-$, $-RuCl_2(O_2CCF_3)Ru-$, $-RuCl(O_2CCF_3)_2Ru-$ and $-Ru(O_2CCF_3)_3Ru-$. In the presence of HCl, (present as an impurity in the CH_2Cl_2 used), any $[O_2CCF_3]^-$ ligands are displaced and the tri-μ-chloro complex forms. In support of this suggestion $Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)$ reacts in CH_3NO_2 with anhydrous HCl to form the cation $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$, as well as some $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$. Also it was found that the hydroxo and alkoxo complexes described earlier react with HX (X = Cl, Br, I) to give the cationic $[Ru_2(\eta\text{-arene})_2X_3]^+$ and dimeric $[Ru(\eta\text{-arene})X_2]_2$ products (see section 2.6).

Crystal structure of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4].MeOH$

Details of the solution of the structure are given in the experimental section. Final atomic parameters are given in Table 2.6 and selected bond distances and angles in Table 2.7. There are two crystallographically independent binuclear cations each lying across a two-fold rotational axis. There are no significant differences in bond lengths and angles between the two cations. The apparent shortening of the Ru-Cl bonds in cation A is likely to result from the high anisotropic thermal parameters of

the bridging chlorines (see Figure 2.10). The Ru...Ru distance of 3.283 Å is in the middle of the expected Ru...Ru binuclear range of 3.44 to 3.08 Å [101,102]. Both ruthenium atoms are in oxidation state II which precludes any metal-metal bonding. The Ru-Cl bond lengths lie between 2.41 and 2.45 Å with Ru-Cl-Ru' angles in the range 84° to 86° and Cl-Ru-Cl angles of 79 (±1°). These values are in close agreement with the values found in other trichloro bridged species.

The ring centroids of the π-bonded p-cymene groups are 1.647 Å and 1.642 Å from the ruthenium atoms of cations A and B respectively. This compares with a value of 1.637 Å in di-μ-chloro-bis[chloro(η-p-cymene)Os(II)] [6]. All C-C single bonds refined to within 0.01 Å of their idealised value of 1.54 Å. In neither cation A nor cation B are the isopropyl groups symmetrical with respect to the benzene ring. Cation A has a torsion angle C(2)-C(3)-C(8)-C(9) = 26° which is identical to the conformation of the p-cymene in the osmium complex[6]. Cation B however shows the corresponding torsion angle C(16)-C(15)-C(18)-C(19) = 57°. The disordered solvent molecule shows no close intermolecular contacts.

The structure of one of the cations is shown in Figure 2.9, an ORTEP diagram of the central "Ru_2Cl_3" unit in Figure 2.10 and a cell packing diagram in Figure 2.11.

Figure 2.9 The molecular structure of the cation $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3]^+$

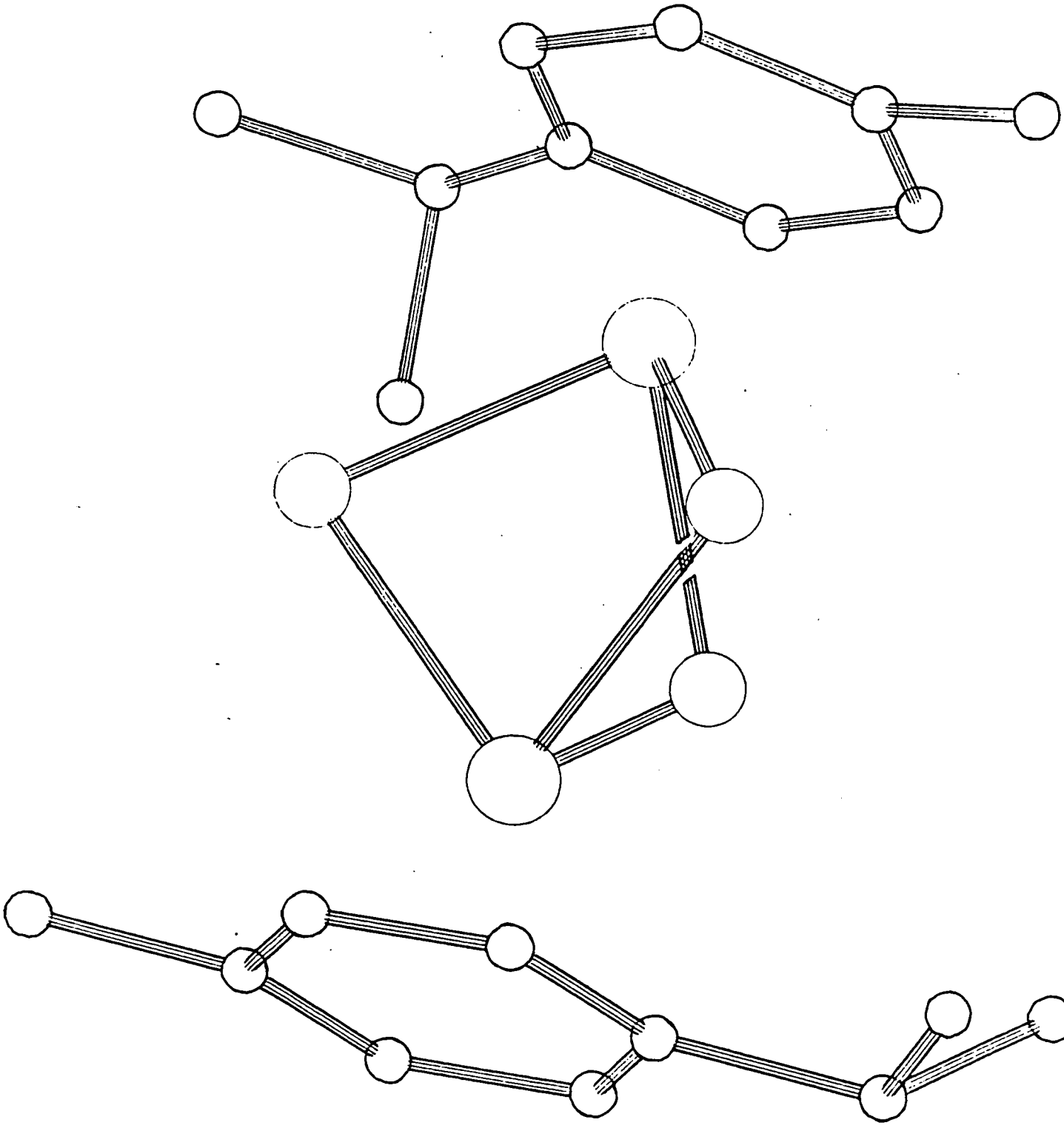


Figure 2.10 An ORTEP diagram of the central "Ru_2Cl_3" unit showing the nature of the rotational disorder

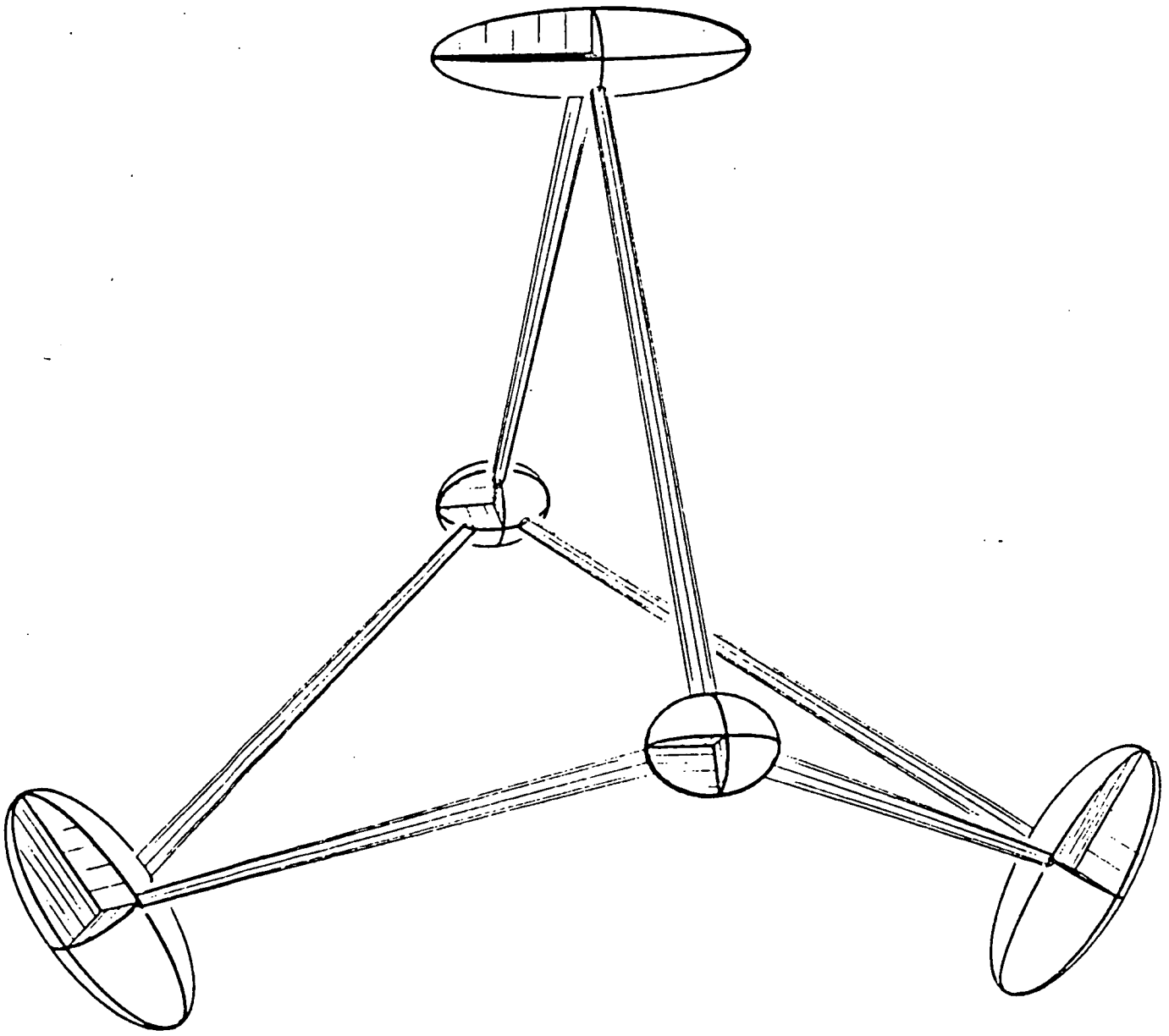
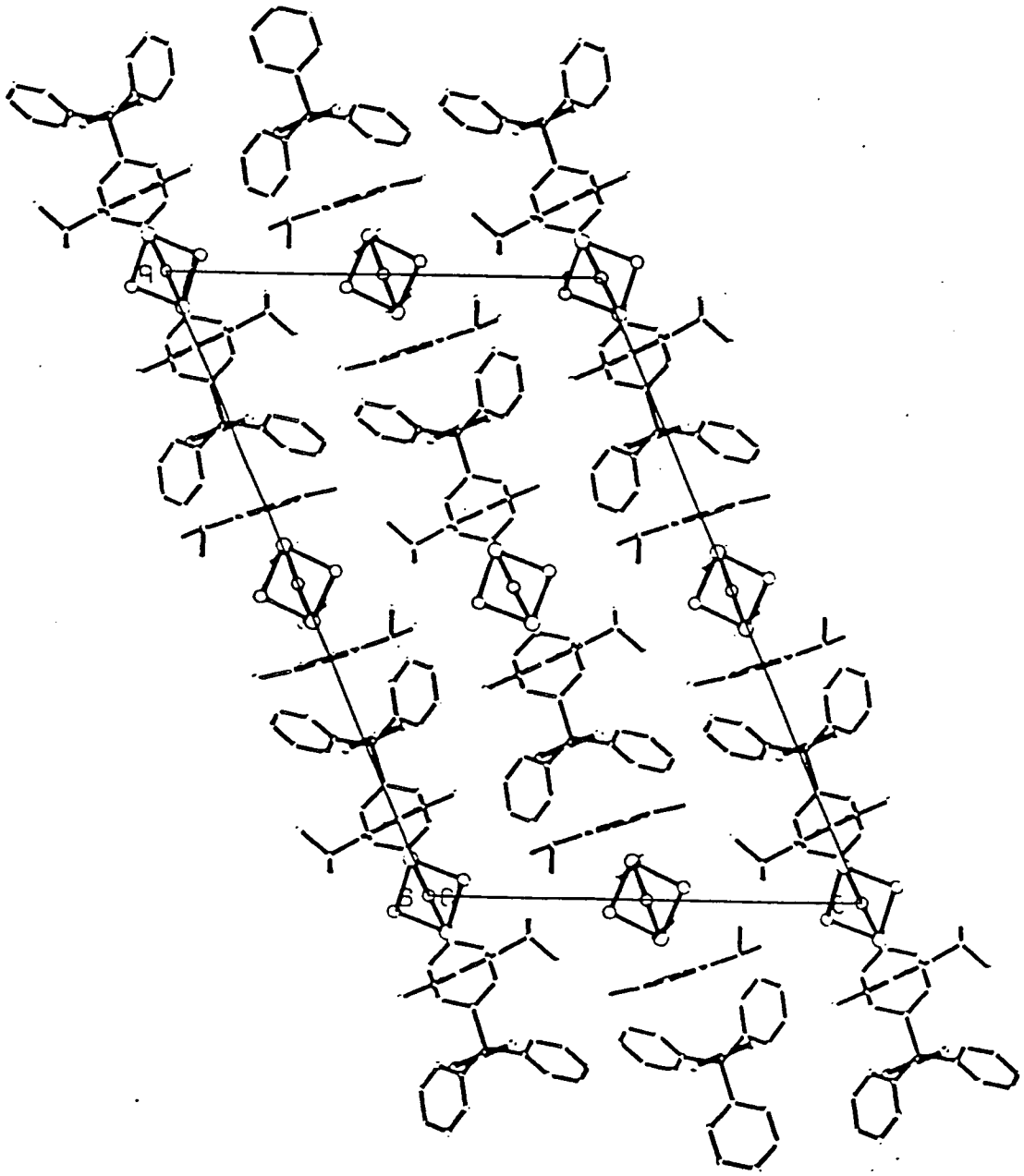


Figure 2.11 A cell packing diagram for $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4].MeOH$

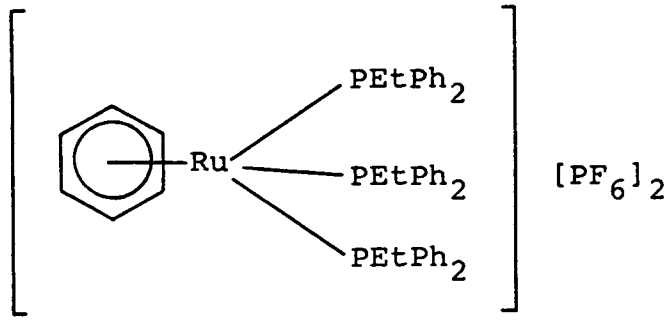


2.6 Some reactions of hydroxo and alkoxo bridged species

The stability of hydroxo bridges in cationic complexes has been previously demonstrated by their resistance to cleavage under conditions in which halide bridges are normally broken, e.g. $[Pt_2(OH)_2(PR_3)_4][BF_4]_2$ does not react with more PR_3[103]. The inert nature of these bridges in the complexes $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]\cdot 2Me_2CO$[82] and $[Ru_2(\eta\text{-arene})_2(OH)_3][BPh_4]$[84] (arene = 1,4-$MeC_6H_4CHMe_2$, 1,3,5-$C_6H_3Me_3$) is demonstrated by the fact that no reaction with tertiary phosphines is observed even under prolonged refluxing. This lack of reactivity towards Lewis bases might, in the case of the triple hydroxo bridged complexes, be due to the presence of substantial intra-molecular hydrogen bonding interactions. In the case of the benzene complex, the high stability may be due to inter-molecular hydrogen bonding interactions with the acetone solvent molecules, analogous to those present in the solid state; or perhaps more probably, to strong steric interactions between the π-bonded benzene rings and the bulky tertiary phosphine ligands in any transition state.

If these assumptions are correct, then the analogous $[Ru_2(\eta\text{-arene})_2(OR)_3]X$ (R = Me, Et; arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, 1,3,5-$C_6H_3Me_3$; X = BPh_4, PF_6) where such interactions are not possible would be expected to cleave readily. At the time of writing only a

preliminary study of these reactions has been made but, in general, no bridge cleavage occurs when the complex $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][PF_6]$ (39) is reacted with a nitrogen donor ligand, (pyridine, 2,2'-bipyridyl or 1,10-phenonthroline), even under reflux conditions for periods of up to six hours. No reaction is observed between PPh_3 and (39) in acetone under reflux conditions but reaction of this complex with $PEtPh_2$ in MeOH gives a small amount of an orange crystalline solid. The infrared spectrum of this complex contain bands attributable to both the tertiary phosphine ligand and $[PF_6]^-$. The ^1H n.m.r. spectrum in $(CD_3)_2SO$ had a singlet resonance at δ5.73 ppm attributable to the protons of the $\eta\text{-}C_6H_6$ ligand as well as resonances typical of $PEtPh_2$ and integration of the signals was in a ratio $PEtPh_2:C_6H_6$ of ca. 3:1. The $^{31}P\text{-}\{^1H\}$ spectrum showed a singlet at δ25.15 ppm indicating that all the phosphine ligands were magnetically equivalent, as well as the $[PF_6]^-$ septet centred at δ-143 ppm. The complex is best formulated as the dicationic complex $[Ru(\eta\text{-}C_6H_6)(PEtPh)_3][PF_6]_2$ (40). Analytical data is in close agreement with this formulation but unfortunately, attempts to determine the structure unequivocally by means of X-ray analysis were unsuccessful due to extensive disorder in the crystals. However, complexes of this type have already been reported in the literature although not with this particular tertiary phosphine[19].



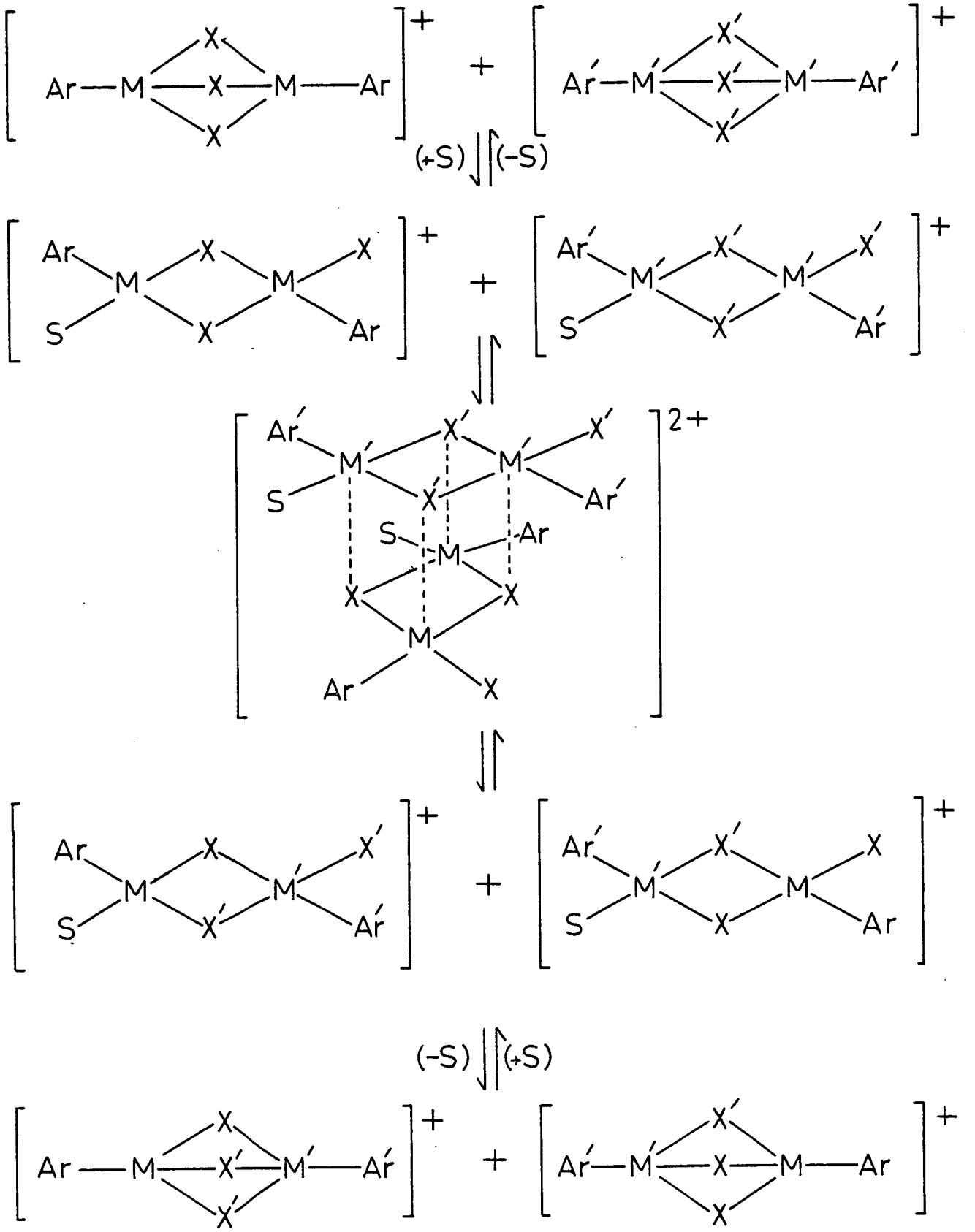
(40)

Complex (39) also reacts with a variety of other tertiary phosphines (PMe_2Ph, $PEtPh_2$ etc.) and with $P(OMe)_3$ but in these reactions a mixture of products is produced (n.m.r. evidence), and attempts to isolate pure compounds were unsuccessful.

Previously, it has been shown that mixing equimolar amounts of $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BF_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3][BF_4]$ in $(CD_3)_2CO$ at ambient temperature led to the formation of the mixed halide complexes $[Ru_2(\eta\text{-}C_6H_6)_2Cl_2Br][BF_4]$ and $[Ru_2(\eta\text{-}C_6H_6)ClBr_2][BF_4]$, which were present as part of an inseparable statistical mixture of the four compounds[9]. This reaction was extended to the formation of hetero-bridged, heteroarene and heteronuclear triple halide bridged arene complexes of ruthenium(II) and osmium(II). A possible mechanism (see Scheme 2.10) was proposed to account for this scrambling process which involves partial bridge cleavage by the solvent and a tetranuclear transition state.

In an attempt to discover the limitations of this scrambling process, the reactions of hydroxo and alkoxo bridged complexes with triple chloro bridged arene complexes and with other hydroxo and alkoxo complexes have been investigated.

Scheme 2.10 A possible mechanism for bridge scrambling



Unfortunately most of the reactions investigated did not proceed in the straightforward manner expected. Thus, in the reactions between $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$ and a variety of hydroxo and alkoxo bridged complexes, the ^1H n.m.r. spectra of the reaction mixture contained a greater number of resonances than would have been predicted if the simple scrambling mechanism, shown in Scheme 2.10, had been the only process operating. These additional peaks in the ^1H n.m.r. spectra may be due to monomeric species of the type $Ru(\eta\text{-}C_6H_6)Cl(OH)S$, $[Ru(\eta\text{-}C_6H_6)Cl_2(OH)]^-$ _etc._, ($S = CD_3NO_2$ or $(CD_3)_2SO$), although there is no positive evidence for this. Similarly, studies involving $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and a variety of halo and alkoxo η-benzene ruthenium(II) complexes gave more complex ^1H n.m.r. spectra than predicted. A possible explanation for this may lie in the fact that both the parent complex and $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$, which is formed in wet CD_3NO_2 solution, may be exchanging and hence twice as many lines as predicted are observed. Interestingly no exchange was observed between $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$, even upon prolonged interaction, _i.e._ unlike the analogous halide complexes no heteroarene complex, $[(\eta\text{-}C_6H_6)Ru(OH)_3Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)][BPh_4]$, was formed.

Some success has however been achieved in preparing mixed alkoxo bridged complexes. The ^1H n.m.r. spectrum in $(CD_3)_3SO$ of an aged solution of a mixture of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$

shows four distinct sets of resonances. A singlet, quartet and triplet, at δ5.42, 4.50 and 1.38 ppm respectively are due to the $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3]^+$ cation, while two singlets at δ5.47 and 4.34 ppm, in the ratio 4:3, are due to the $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$ cation. Two additional singlets in the η-benzene range, at δ5.40 and 5.37 ppm, two singlets in the o-methyl range, at δ4.30 and 4.26 ppm, and additional quartets, at δ4.41 and 4.10 ppm, and triplets, at δ1.06 and 0.90 ppm, can be assigned to the hetero-bridged complexes $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_2(OEt)][BPh_4]$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)(OEt)_2][BPh_4]$. The mixed metal complex $[OsRu(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ is prepared by addition of a CD_3NO_2 solution of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ to a solution of $[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$. The ^1H n.m.r. spectrum in CD_3NO_2 initially shows four singlet resonances. Peaks at δ5.40 and 4.42 ppm are assigned to the former complex, while those at δ6.03 and 4.59 ppm are due to the latter. On leaving the solution, new resonances appear at δ6.01, 5.43 and 4.47 ppm, which can be assigned to the heterometallic complex $[OsRu(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$. The mechanism postulated previously for the exchange of the halide bridged complexes (see Scheme 2.10) is equally valid for the exchange processes described above.

The mechanism postulated for the reaction of the hydroxo bridged complexes with alcohols involved initial protonation of the hydroxyl ligand and subsequent bridge cleavage. Further evidence for this initial step is provided by a study of the reactions of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$

with anhydrous HX (X = Cl, Br, I). If anhydrous HCl is bubbled through a solution of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ in CH_3NO_2, then the initial orange solution darkens and a red precipitate is formed. The red precipitate is readily identified as the dimer $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$. When the solvent is removed from the remaining solution and the residual gum treated with a methanolic solution of $Na[BPh_4]$, then the well-known complex $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3][BPh_4]$ is obtained. Substitution of HX (X = Br, I) for HCl leads to the formation of the insoluble $[Ru(\eta\text{-}C_6H_6)X_2]_2$ in quantitative yield. If these reactions are repeated with $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ the products obtained are identical. However, when these reactions are carried out using $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ then the product distribution is somewhat different. Reaction with HCl now only gives the cationic product, $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4]$, whilst reaction with HBr gives both $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Br_3][BPh_4]$ and the dimer $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Br_2]_2$, and reaction with HI results in the formation of only $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)I_2]_2$. Thus, the nature of the product depends only on the extent to which the arene ring confers solubility on the species formed. These reactions are not unique, since it has previously been shown that various binuclear hydroxide ruthenium(II) phosphine complexes react with HX to give the analogous halide species[100].

This facile protonation of the hydroxo bridged complexes is useful in that it allows the preparation of a variety of ruthenium(II) bisarene complexes without requiring the use of an expensive silver reagent[42] (see Section 1.1). Although only preliminary investigations have been made to date, these indicate that the successful preparation of a wide range of ruthenium(II) bisarene complexes should be possible using this route.

Hence, stirring $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ in a mixture of $(CH_3)_2CO/CF_3CO_2H$ (1:1 v/v) for 10-15 minutes gives a pale yellow solution, which after removal of solvent and subsequent treatment with first $C_6H_6/(CH_3)_2CO$ (1:1 v/v) and then a methanol solution of $Bu_4N[BF_4]$, gave an off-white precipitate. The ^1H n.m.r. spectrum of this solid in $(CD_3)_2SO$ showed only a single resonance at δ6.89 ppm characteristic of $[Ru(\eta\text{-}C_6H_6)_2][BF_4]_2$. Similarly if $[Ru(\eta\text{-}C_6H_6)((CH_3)_2CO)_3]^{2+}$, generated *in situ* from $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)]^+$ and $(CH_3)_2CO/CF_3CO_2H$, is treated with $1,3,5\text{-}C_6H_3Me_3/(CH_3)_2CO$, then the ^1H n.m.r. spectrum in $(CD_3)_2SO$ contains three resonances at δ6.93, 6.86 and 2.37 ppm in the ratio 1:2:3 which is consistent with the previously reported parameters for $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)][BF_4]_2$. Although an extensive study has not been carried out, these preliminary investigations indicate that the preparation of ruthenium(II)bisarene complexes by this route would be a viable alternative to the more traditional synthesis.

Finally a brief study of the reactions of $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ and $[Ru_2(\eta\text{-}C_6H_6)(OMe)_3][PF_6]$ with $Na[BH_4]$ in $(CD_3)_2SO$ was made. A free benzene resonance, at δ7.10 ppm, in the ^1H n.m.r. spectra of both sets of reaction products indicates that a significant amount of displacement of the arene occurs. Both spectra also had peaks characteristic of an η^5-cyclohexadienyl as well as the normal η^6-benzene resonance, indicating that hydride addition had only occurred at one of the arene rings. The major peak however in both spectra occurred at δ-11.26ppm and this may be attributed to a Ru-H resonance. As there was no benzene or cyclohexadienyl peaks of comparable intensity then the major product may be a $(CD_3)_2SO$ complex of the type $Ru((CH_3)_2SO)_4H_2$ or $[Ru((CH_3)_2SO)_3H_3]X$. Unfortunately, it proved impossible to isolate any of the complexes observed in solution in a pure state and considerably more work would be required before all the ruthenium species present are fully characterised.

In conclusion, it has been shown that these binuclear arene ruthenium(II) complexes undergo a variety of interesting reactions. Unfortunately, however, the most successful reactions give products which have previously been synthesised by alternate routes although several new species have been observed.

2.7 Experimental

Micro-analysis, infrared spectra, melting point and conductivity measurements were obtained as described in Section 1.5. Hydrogen-1-n.m.r. spectra were recorded on Bruker WP-80 and WP-200 spectrometers.

Materials

As in Chapter 1 together with $Pb(SEt)_2$ prepared from lead tetraacetate and ethanethiol[104] and anhydrous hydrogen halides prepared by standard literature methods[105].

Microanalytical and conductivity data are presented in Table 2.1, while hydrogen-1-n.m.r. data are given in Table 2.2.

Crystal structure determination of $[Ru_4(\eta\text{-}C_6H_6)_4(\mu_2\text{-}OH)_4(\mu_4\text{-}O)][BPh_4]_2.2Me_2CO$

Crystals suitable for X-ray analysis were obtained by recrystallisation of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ from acetone. Data was collected on a crystal of dimensions 0.7 x 0.12 x 0.12 mm, in the ω-2θ scan mode using a CAD-4 diffractometer with monochromated $M_o - K_\alpha$ radiation for θ out to 22°.

Crystal Data: $Ru_4C_{78}H_{76}B_2O_7$, M = 1551, a = 13.267(8), b = 12.227(3), C = 41.864(8) Å, β = 98.23(3)°, V = 6721 Å^3, D_m = 1.50, D_c = 1.53 g cm^{-3}, z = 4, $\mu(M_o - K_\alpha)$ = 9.2 cm^{-1}, $\lambda(M_o - K_\alpha)$ = 0.71069 Å. The space group is $P2_{1/c}$.

Intensities were measured for 8175 independant reflections of which 3110 had $I > 2.5\sigma(I)$. No crystal decay was observed and an empirical absorption correction was applied.

Structure, solution and refinement

The four ruthenium atoms were located using direct methods[106] and all the remaining non-hydrogen atoms were found from subsequent Fourier syntheses. Refinement of the structure by least squares reduced the R-factor to 0.080 in 5 cycles with Ru and O atoms refined anisotropically and the phenyl groups of the tetraphenylborate anions constrained to be idealised planar hexagons. Because of the large number of atoms in the structure, hydrogen atoms were not included in the structure factor calculation in the usual way. Instead,

the data were modified to allow for hydrogen atoms in idealised positions (C-H = 1.1 Å), and refinement continued on the modified data[107]. At convergence based on unmodified data, R = 0.076 (Rw = 0.085). The maximum shift/esd at this stage was 0.031. The strongest peak on a difference map had a height of about 1 $e\text{Å}^{-3}$ near one of the benzene rings in the cation.

Final fractional coordinates are given in Table 2.3 and selected bond distances and angles in Table 2.4. The structure of the cation is shown in Figure 2.1, and ORTEP diagram of the central "Ru_4O_5" unit in Figure 2.2 and a cell packing diagram in Figure 2.3.

Crystal structure determination of $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$

Crystals suitable for X-ray analysis were obtained by the method given (see below). An orange cubic crystal of edge 0.05 mm was chosen. Accurate cell dimensions were obtained by least squares refinement of 24 reflections measured on a Nonius CAD4 diffractometer with monochromatised $M_o - K_\alpha$ radiation.

Crystal Data: $Ru_4C_{24}H_{52}O_{24}S_2$, M = 1193, a = 12.405(1) Å, V = 1909 Å, D_c = 2.08 g cm^{-3}, D_m = 2.10 g cm^{-3} (by flotation), z = 2, $\mu(M_o - K_\alpha)$ = 17.1 cm^{-1}, $\lambda(M_o - K_\alpha)$ = 0.71069 Å. The space groups is Pn2m.

Intensities were measured for 1741 reflections to $2\theta = 70^{\circ}$, and these were reduced to 416 independant data including 48 systematic absences. The merging gave an estimated R-factor of 0.043 and no indication of deviation from cubic symmetry. No absorption correction was applied.

Structure, solution and refinement

The refinement was based on the 245 reflections with $I > 3\sigma(I)$. The structure was solved by conventional Patterson and difference Fourier techniques. In the cation, which is centred at 1/4, 1/4, 1/4, the Ru and O atoms were refined anisotropically. The coordinated benzene is disordered over two positions and in the refinement, these rings were given a fixed site occupancy of 0.5 and were constrained to be identical regular hexagons. Hydrogen atoms for the benzene ring and for the hydroxyl group were included in the refinement in fixed positions to give C-H = 1.10 Å, and O-H = 1.02 Å.

The sulphate anions were also disordered with the sulphur atom and one of the oxygens lying along the three-fold axis and having essentially two-fold disorder, while the position of the other atoms is much less defined. For refinement, the ions were constrained to be a set of interpenetrating regular tetrahedra with S-O fixed at 1.48 Å. The water molecules are poorly defined and only show on the difference electron density syntheses as broad peaks in the channels intersecting at 1/4, 1/4, 3/4 and symmetry related positions. Best refinement occurred with half occupancy of three independant sites. This accounts for

10½ of the 12 water molecules required by the empirical formula, but can only be taken as an approximate indication of the positions occupied by water molecules in the crystal.

For the final cycles, a weighting scheme of $W = 1.0$ for $\underline{F}_o$ 100, $W^{\frac{1}{2}} = 100/\underline{F}_o$ otherwise was used. At convergence, based on 22 adjustable parameters, $R = 0.048$, $R_w = 0.058$. An analysis of agreement showed good uniformity except for reflections with low sin θ values, where poor modelling of the disordered water would be most serious. The SHELX[74] program was used for all crystallographic calculations.

Figure 2.5 shows the molecular structure of the cation and Table 2.5 contains the final fractional coordinates.

Crystal structure determination of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4\text{-}CHMe_2)_2Cl_3][BPh_4].MeOH$

Dark red needle crystals were grown from a 313-333 K petroleum ether/methylene chloride mixture. A crystal of dimensions 0.15 x 0.15 x 0.25 (needle) mm was mounted along the needle axis. Data was collected in the ω-2θ scan mode using a CAD-4 diffractometer with monochromated $M_o - K_\alpha$ radiation for θ out to 25°.

Crystal Data: $Ru_2C_{44}H_{48}BCl_3.CH_3OH$, M = 928, monoclinic, I2 (non standard setting of C2), a = 27.331(5), b = 9.765(5), c = 16.923(2) Å, β = 112.748(14)°, V = 4165 Å^3, D_m = 1.46, D_c = 1.48 g cm^{-3}, z = 4, μ(M_o - K_α) = 9.3 cm^{-1}, λ(M_o - K_α) = 0.71069 Å.

3869 unique reflections were measured of which 2783 had I > 2.5σ(I). No crystal decay was observed and no absorption correction was applied.

Structure, solution and refinement

The two Ru atoms were located from a Patterson map and all remaining non hydrogen atoms were found from subsequent Fourier maps. The structure consists of two crystallographically unrelated cations. Each Ru...Ru bond is bisected by a two-fold rotation axis which also runs through the apical Cl. One of these molecules was found to be rotationally disordered about the Ru...Ru axis. Disorder was apparent in one of the phenyl rings of the tetraphenylborate anion and also in the position of the methanol solvent molecule. Smooth convergence of this partially disordered structure was facilitated using a constrained least squares refinement in which all phenyl groups were input as idealised planar rings with C-C bond lengths of 1.395 Å. All other C-C bonds were constrained to 1.54 Å with a weight of 0.01[74]. Hydrogen atoms bonded to phenyl groups were included in their calculated positions with a common fixed temperature factor of U = 0.08 Å^2. In the final cycles of

refinement the two independent ruthenium atoms and four independent chlorine atoms were refined anisotropically. All other non-hydrogen atoms were given individual isotropic temperature factors providing a total of 163 refinable parameters. The weighting scheme applied was $w = 1/(\sigma^2(F_o) + 0.0009\ F_o^2)$ and the final R factor was $R = 0.064$, $R' = 0.083$ for the 2783 observed data. A final difference map showed five peaks each of about $1\ e\ \text{Å}^{-3}$ which occurred near the disordered MeOH solvent molecule, near the rotationally disordered bridging chlorines of cation B, and near the disordered phenyl group of the tetraphenyl borate.

Final fractional coordinates are given in Table 2.6 and bond lengths and angles in Table 2.7. The molecular structure of one of the cations is shown in Figure 2.9, the nature of the rotational disorder in Figure 2.10 and a cell packing diagram in Figure 2.11.

"Di-μ-hydroxo(aqua)hydroxo-bis[(η-benzene)ruthenium(II)] tetraphenylborate"

Addition of an excess of $Na[BPh_4]$ (0.20 g; 0.60 mmol) in water (5 ml) to the yellow solution obtained from the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.20 mmol) and NaOH (0.15 g; 0.40 mmol) in warm water (20 ml) gave a pale yellow precipitate which was filtered off and air-dried. The filtrate deposited more of the complex if left to stand (yield 90 mg; 65%), m.p. 190°C (decomp.),

[ν(OH) 3520, 3615 cm^{-1}; ν(Ru-OH) 1135 cm^{-1}; ν(RuO) 490 cm^{-1} (mull)]. [$^{13}C-\{^{1}H\}$ n.m.r. in CD_3NO_2 (298 K): δ77.8(s) ppm, δ121-136 ppm $[BPh_4]^-$]: slope of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ plot in CH_3NO_2 = 116.

A small amount of tetra-μ_2-hydroxo-μ_4-oxotetrakis-[(η-benzene)ruthenium(II)]tetraphenylborate acetone solvate (1/2) is also precipitated from this solution as evidenced by infrared [ν(OH) 3530 cm^{-1} (mull)] ^1H n.m.r. (CD_3NO_2) [δ5.57(s) ppm weak] and $^{13}C-\{^{1}H\}$ n.m.r. [δ79.4 ppm; δ121-136 ppm $[BPh_4]^-$] data. Recrystallisation of this product from acetone gives a pure sample of the latter (m.p. 185°C (decomp.)) [ν(OH) 3530 cm^{-1}; ν(CO) 1695 cm^{-1}; ν(Ru-OH) 1135 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)], $^{13}C-\{^{1}H\}$ n.m.r. in CD_3NO_2 (298 K): δ79.4(s) ppm. Alternatively, the complex $[Ru(\eta-C_6H_6)Cl_2]_2$ (0.10 g: 0.20 mmol) was dissolved in warm water (5 ml) and filtered. The orange solution was shaken with an excess of Na_2CO_3 (0.20 g; 2.0 mmol) for 2 hours to give a yellow solution, which on addition of $Na[BPh_4]$ (0.20 g; 2.0 mmol) gave the complex as a yellow precipitate (yield 80 mg; 59%). Recrystallisation from acetone then gave pure $[Ru_4(\eta-C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$.

Tetra-μ_3-hydroxotetrakis[η-benzene ruthenium(II)]-sulphate hydrate (1/12): the complex $[Ru(\eta-C_6H_6)Cl_2]_2$ (0.20 g; 0.40 mmol) was dissolved in water (10 ml) and the orange solution was filtered. An excess of Na_2SO_4

(0.20 g; 1.50 mmol) was then added, the solution shaken vigorously for 10 minutes and then Na_2CO_3 (0.08 g; 0.80 mmol) added. On further vigorous shaking for 24 hours, the orange crystalline solid was deposited from solution, m.p. 200°C (decomp.) (0.07 g; 31%). Alternatively, an aqueous solution of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.20 g; 0.40 mmol) in water (10 ml) was shaken with $AgNO_3$ (0.27 g; 1.60 mmol). After filtering off the AgCl, the orange/yellow solution was treated as above with Na_2SO_4 (0.20 g; 1.50 mmol) and then Na_2CO_3 (0.08 g; 0.80 mmol) to give orange crystals (yield 140 mg; 60%) [ν_{OH} 3250 cm^{-1}; δ_{HOH} 1640 cm^{-1}; $\nu_{(S-O)}$ 1060, 610, 975 and 478 cm^{-1}].

"μ-Bromo(di-μ-hydroxo)bis[(η-benzene)ruthenium(II)]-hexafluorophosphate hydrate (1/2)":- The complex $[\{Ru(\eta\text{-}C_6H_6)OH\}_4][SO_4]_2.12H_2O$ (0.10 g; 0.08 mmol) was suspended in water and LiBr (0.015 g; 0.16 mmol) was added giving an orange solution. Addition of $NH_4[PF_6]$ (0.05 g; 0.40 mmol) gave an orange-yellow precipitate m.p. 170°C (decomp.) (yield 50 mg; 51%) [ν_{OH} 3640, 3580 cm^{-1}; $\nu_{OH(H_2O)}$ 3300 cm^{-1}; δ_{HOH} 1630 cm^{-1}] Found: C, 21.6; H, 2.4; Br, 12.9 Calc. for "$C_{12}H_{18}BrF_6O_4PRu_2$":- C, 22.0; H, 2.7; Br, 12.3%.

"μ-Bromo(di-μ-hydroxo)bis[(η-benzene)ruthenium(II)]tetraphenylborate:- was similarly prepared from $[\{Ru(\eta\text{-}C_6H_6)OH\}_4][SO_4]_2.12H_2O$, LiBr and $Na[BPh_4]$. [Found: C, 54.8; H, 4.4 Calc. for "$C_{36}H_{34}BBrO_2Ru_2$": C, 54.6; H, 4.3%]
^1H n.m.r. in $(CD_3)_2CO$ at 298 K:- 5.92(s) ($-\mu Br_3-$); 5.88(s) ($-(\mu OH)(\mu\text{-}Br_2)-$); 5.70(s) ($-(\mu OH_2)(\mu Br)-$; 5.52(s) ($-\mu(OH)_3)-$; 6.90-7.60(m) $[BPh_4]^-$.

Tri-μ-hydroxobis[(η-hexamethylbenzene)ruthenium(II)]-chloride hydrate (1/4):- The compound $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.10 g; 0.15 mmol) was dissolved in hot water (20 ml). The solution was filtered, an excess of NaOH (0.30 g; 8.0 mmol) added and the solution refluxed for two hours. On cooling a pale green solid was deposited which was filtered off, washed with water and air dried (yield 80 mg; 78%) m.p. 192-195°C [ν(OH) 3420 cm^{-1}; ν(HOH) 1660 cm^{-1}; ν(RuO) 500 cm^{-1} (mull)].

Tri-μ-methoxobis[(η-hexamethylbenzene)ruthenium(II)] tetraphenylborate:- The compound $[Ru(\eta\text{-}C_6Me_6)Cl_2]_2$ (0.10 g; 0.15 mmol) was added to a freshly prepared solution of NaOMe [Na (ca. 0.20 g) in MeOH (10 ml)]. The mixture was stirred and heated gently to give a yellow solution and addition of $Na[BPh_4]$ (0.07 g; 0.20 mmol) gave a yellow solid which was filtered off and washed with methanol (yield 70 mg; 47%), m.p. 168-172°C [ν(CO) 1050 cm^{-1}; ν(RuO) 495 cm^{-1} (mull)].

Tri-μ-methoxobis[(η-benzene)osmium(II)]tetraphenylborate

The compound $[Os(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.15 mmol) was added to a freshly prepared solution of NaOMe in methanol (10 ml). The mixture was stirred and heated gently to give a clear solution and then addition of $Na[BPh_4]$ (0.07 g; 2.0 mmol) gave a microcrystalline white solid which was washed with methanol and air dried (yield 60 mg; 39%), m.p. 174-176°C [ν(CO) 1048 cm^{-1}; ν(OsO) 400 cm^{-1} (mull)].

Tri-μ-phenoxobis[(η-benzene)ruthenium(II)]tetraphenylborate

The compound $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.20 mmol) was added to an excess of freshly prepared NaOPh in methanol (10 ml) (made from NaOMe and excess phenol in methanol). The mixture was gently heated to give a yellow solution and addition of $Na[BPh_4]$ (0.07 g; 0.20 mmol) gave a yellow solid which was washed with methanol and air dried (yield 100 mg; 52%) m.p. 195-196°C [ν(CO) 1065 cm^{-1}; ν(RuO) 490 cm^{-1} (mull)].

Tri-μ-methoxobis[(η-benzene)ruthenium(II)]tetraphenylborate

The compound $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.20 mmol) was added to a suspension of "80-90% $NaNH_2$" (0.12 g; 3.0 mmol) in CH_3CN (25 ml). This mixture was shaken for 24 hours and then precipitated NaCl and excess "$NaNH_2$" were removed by filtration through celite. The resulting yellow/brown solution was evaporated to dryness on a rotary

evaporator. Treatment of the residue with a methanol (5 ml) solution of $Na[BPh_4]$ (0.14 g; 0.40 mmol) precipitated a yellow microcrystalline solid which was washed with methanol and air dried (yield 90 mg; 58%) m.p. 198°C (decomp.) [ν(CO) 1050 cm^{-1}; ν(Ru-O-C) 1145 cm^{-1}; ν(RuO) 550 cm^{-1} (mull)]. Similarly prepared was Tri-methoxobis[(η-p-cymene)ruthenium(II)]tetraphenylborate from $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (0.12 g; 0.20 mmol) and $NaNH_2/CH_3CN$ (yield 70 mg; 40%), m.p. 151°C [ν(CO) 1045 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)], slope of $\Lambda_o - \Lambda_e$ vs $C^{\frac{1}{2}}$ plot in CH_3NO_2 = 136.

Tri-μ-ethoxobis[(η-benzene)ruthenium(II)]tetraphenylborate

The compound $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.20 mmol) was added to a suspension of "80-90% $NaNH_2$" (0.12 g; 3.0 mmol) in CH_3CN (30 ml). This mixture was shaken for 24 hours and then precipitated NaCl and excess "$NaNH_2$" removed by filtration through celite. The resulting solution was evaporated to dryness and treatment of the residue with an ethanol (3 ml) solution of $Na[BPh_4]$ (0.07 g; 0.20 mmol) precipitated an orange crystalline solid which was washed with ethanol and dried under vacuo (yield 110 mg; 67%) m.p. 220°C (decomp.) [ν(CO) 1050 cm^{-1}; ν(RuO) 570 cm^{-1} (mull)]. Similarly prepared was Tri-μ-ethoxobis-[(η-p-cymene)ruthenium(II)]tetraphenylborate from $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]$ (0.12 g; 0.20 mmol) and $NaNH_2/CH_3CN$ (yield 75 mg; 41%) m.p. 188°C [ν(CO) 1055 cm^{-1}; ν(RuO) 500 cm^{-1} (mull)].

Tri-μ-isobutoxobis[(η-benzene)ruthenium(II)]tetraphenylborate

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)][BPh_4]$ (0.20 g; 0.27 mmol) was warmed gently in iso-butanol (30 ml) for 15 minutes. The microcrystalline golden precipitate was filtered off, washed with diethyl ether and air dried (yield 180 mg; 75%) m.p. 201-203°C (decomp.) [ν(CO) 1050 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)]. Similarly prepared was Tri-μ-isopropoxobis[(η-benzene)ruthenium(II)]-tetraphenylborate from reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3(H_2O)]$-$[BPh_4]$ (0.22 g; 0.30 mmol) in iso-propanol (yield 240 mg; 95%) m.p. 148-150°C (decomp.) [ν(CO) 960 cm^{-1}; ν(RuO) 485 cm^{-1} (mull)]. [^{13}C-{^1H} n.m.r. in CD_3NO_2 (298 K): δ78.8 ppm(s), δ33.8 and 19.7 ppm $OCH(CH_3)_2$; δ121-136 ppm $[BPh_4]^-$].

Tri-μ-ethanethiolatobis[(η-benzene)ruthenium(II)]tetra-phenylborate

The compound $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ (0.10 g; 0.20 mmol) was shaken with $Pb(SEt)_2$ (0.30 g; 0.90 mmol) in CH_3CN (25 ml) for 48 hours. The precipitated $PbCl_2$ was removed by filtration through celite. The resulting yellow/brown solution was evaporated to dryness and the residue dissolved in methanol (5 ml) and treated with $Na[BPh_4]$ (0.14 g; 0.40 mmol) to give a yellow precipitate. This was filtered off, washed with methanol and diethyl ether and dried *in vacuo* at 56°C (yield 90 mg; 52%) m.p. 219-223°C (decomp.) [ν(SC) 610 cm^{-1}; ν(RuS) 365 cm^{-1} (mull)] [^{13}C-{^1H} n.m.r. in CD_3NO_2 (298 K): δ84.5 (s) ppm; δ121-136 ppm $[BPh_4]^-$; δ32.8 and 17.0 ppm (SEt)].

Similarly prepared was Tri-μ-ethanethiolatobis[(η-p-cymene)-ruthenium(II)]tetraphenylborate from $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ (0.12 g; 0.20 mmol) and $Pb(Set)_2$ in CH_3CN. (Yield 110 mg; 57%), m.p. 181°C [ν(SC) 650 cm^{-1}; ν(RuS) 370 cm^{-1} (mull)].

Reactions of hydroxo and alkoxo complexes with anhydrous hydrogen halides

Tri-μ-chlorobis[(η-benzene)ruthenium(II)]tetraphenyl borate

The compound $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ (0.12 g; 0.07 mmol) was dissolved in CH_3NO_2 (10 ml) and HCl gas was passed through the stirred solution for 20 minutes. The red solid formed was filtered off, washed with diethylether and air dried. This product was identified as di-μ-chlorobis[chloro(η-benzene)ruthenium(II)] (yield 30 mg; 42%). The remaining solution was evaporated to dryness and the residue dissolved in methanol (5 ml), addition of $Na[BPh_4]$ (0.14 g; 0.4 mmol) gave an orange precipitate which was filtered off, washed with methanol and air dried (yield 50 mg; 45%).

Di-μ-bromobis[bromo(η-benzene)ruthenium(II)]

The compound $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ (0.12 g; 0.07 mmol) was dissolved in CH_3NO_2 (10 ml) and HBr gas passed through the solution for 20 minutes. The dark precipitate was filtered off, washed with diethyl-ether and air dried (yield 80 mg; 85%). Di-μ-iodobis-[iodo(η-benzene)ruthenium(II)] was similarly prepared from

the hydroxo-bridged compound and HI (yield 110 mg; 91%). The compound di-μ-iodobis[iodo(η-p-cymene)ruthenium(II)] was prepared in a similar manner from $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ and HI (yield 120 mg; 72%). Substitution of the compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ for $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$ gives identical products in similar yields.

Tri-μ-chlorobis[(η-p-cymene)ruthenium(II)]tetraphenylborate

The compound $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ (0.15 g; 0.17 mmol) was dissolved in CH_3NO_2 (10 ml) and HCl gas passed through the solution for 20 minutes. The solvent was removed under vacuo and the residue redissolved in methanol (5 ml). Addition of $Na[BPh_4]$ (0.14 g; 0.4 mmol) gave an orange precipitate which was filtered off, washed with methanol and air dried (yield 0.12 mg; 75%).

Tri-μ-bromobis[(η-p-cymene)ruthenium(II)]tetraphenylborate was prepared similarly by passing HBr gas through a solution of $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OH)_3][BPh_4]$ (0.15 g; 0.17 mmol) in CH_3NO_2 (10 ml) (yield 60 mg; 34%). Di-μ-bromobis-[bromo(η-p-cymene)ruthenium(II)], which was also formed in this reaction was removed by filtration prior to evaporation of the solvent (yield 75 mg; 56%).

(η-benzene)tris(ethyldiphenylphosphine)ruthenium(II)-hexafluorophosphate

The compound $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][PF_6]$ (0.20 g; 0.33 mmol) was refluxed in methanol (30 ml) with $PEtPh_2$ (0.30 g; 1.40 mmol) for 4 hours. The solvent was removed and the gummy residue redissolved in a little methanol (5 ml). Diethyl ether (5 ml) was added and the solution left at 0°C for 48 hours. The orange crystalline deposit was filtered off, washed with diethyl ether and dried under vacuo at 56°C (yield 30 mg; 4%), m.p. 208°C.

Table 2.1 Analytical and Conductivity Data for some ruthenium(II) and osmium(II) complexes[a]

	%C	%H	Λ_m
$[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$	59.7(60.2)	5.2(5.2)	116
$[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$[c]	24.9(24.2)	3.6(3.8)	198[d]
$[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Cl.4H_2O$	41.1(42.1)	6.5(6.9)	50[e]
$[Ru_2(\eta\text{-}C_6Me_6)_2(OMe)_3][BPh_4]$	65.4(65.2)	7.3(7.0)	54
$[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$	48.1(49.3)	4.8(4.3)	54[e]
$[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh]_4$	60.5(60.8)	5.3(5.3)	68
$[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$	61.9(62.1)	5.8(5.8)	50
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OMe)_3][BPh_4]$	63.1(63.9)	6.2(6.5)	56
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OEt)_3][BPh_4]$	64.1(64.9)	6.7(6.9)	
$[Ru_2(\eta\text{-}C_6H_6)_2(OPh)_3][BPh_4]$	67.6(67.8)	5.2(5.0)	52[e]
$[Ru_2(\eta\text{-}C_6H_6)_2(SEt)_3][BPh_4].MeOH$	56.9(57.8)	5.6(5.8)	48
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$	60.3(61.7)	6.3(6.5)	48

Table 2.1 (contd.)

	%C	%H	Λ_m
$[Ru_2(\eta\text{-}C_6H_6)_2(O\text{-}Bu^i)_3][BPh_4]$	64.4(64.2)	6.6(6.6)	54
$[Ru_2(\eta\text{-}C_6H_6)_2(O\text{-}Pr^i)_3][BPh_4]$	63.4(63.2)	6.4(6.3)	52
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Br_3][BPh_4]$	51.2(51.3)	4.6(4.7)	64
$[Ru(\eta\text{-}C_6H_6)Br_2]_2$	21.0(21.3)	2.0(1.8)	-
$[Ru(\eta\text{-}C_6H_6)Br_2]_2$	21.0(21.3)	2.0(1.4)	-
$[Ru(\eta\text{-}C_6H_6)(PEtPh_2)_3][PF_6]_2$	52.1(51.8)	4.6(4.6)	119

(a) Calculated values in parentheses

(b) Molar conductivities (S cm^2 mol^{-1}) measured in CH_3NO_2 (unless otherwise stated)

(c) %O 30.4(32.2); %S 4.7(5.4)

(d) Measured in water

(e) Measured at 5 x 10^{-4} mol dm^{-3} concentration

Table 2.2 Hydrogen-1 n.m.r. data for some areneruthenium(II) and osmium(II) complexes at 298 K

Compound	Solvent	η-Arene	Other
$[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$	CD_3NO_2	5.57(s)	2.60(s,OH) 2.10(s,Me_2CO)
$[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Cl.4H_2O$	CD_3NO_2	2.05(s)	c
$[Ru_2(\eta\text{-}C_6Me_6)_2(OMe)_3][BPh_4]$	$CDCl_3$	1.97(s)	4.00(s, OMe)
$[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$	$(CD_3)_2CO$	6.15(s)	4.63(s, OMe)
$[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$	$(CD_3)_2CO$	5.48(s)	4.42(s, OMe)
$[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3][BPh_4]$	$(CD_3)_2SO$	5.43(s)	4.50(q, CH_2) 1.35(t,CH_3, $^3J_{CH_2CH_3}$ 7.0 Hz)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OMe)_3][BPh_4]$	CD_3NO_2	5.24(H_AH_B 18Hz; J 7.0 Hz) 2.82(sp $C\underline{H}Me_2$) 2.20(s,CH_3) 1.32(d,CH_3 of $CHMe_2$ J 7.0 Hz)	4.49(s, OMe)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(OEt)_3][BPh_4]$	CD_3NO_2	5.21(H_AH_B 26Hz; J 6.0 Hz) 2.79(sp $C\underline{H}Me_2$) 2.18(s,CH_3) 1.31(d,CH_3 of $CHMe_2$ J 7.0 Hz)	4.60(q,CH_2) 1.50(t,CH_3, $^3J_{CH_2CH_3}$ 7.0Hz)

Table 2.2 (contd.)

$[Ru_2(\eta\text{-}C_6H_6)_2(OPh)_3]BPh_4]$	CD_3NO_2	5.12(s)	6.95(m) (d)
$[Ru_2(\eta\text{-}C_6H_6)_2(SEt)_3][BPh_4]$	$(CD_3)_2SO$	5.69(s)	2.35(q,CH_2) 1.30(t,CH_3, $^3J_{CH_2CH_3}$ 7.4 Hz)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2(SEt)_3][BPh_4]$	$CDCl_3$	4.74(H_AH_B 21Hz: J 7.0Hz) 2.55(sp $C\underline{H}Me_2$) 1.93(s,CH_3) 1.21(d,CH_3 of $CHMe_2$ J 7.0 Hz)	4.37(q,CH_2) 1.35(t,CH_3, $^3J_{CH_2CH_3}$ 7.4 Hz)
$[Ru_2(\eta\text{-}C_6H_6)_2(O\text{-}Bu^i)_3][BPh_4]$	CD_3NO_2	5.36(s)	1.12(d,CH_3 J 7.0Hz) 4.27(d, CH_2) 2.28(m, CH)
$[Ru_2(\eta\text{-}C_6H_6)_2(O\text{-}Pr^i)_3][BPh_4]$	CD_3NO_2	5.46(s)	4.89(sp, CH) 1.48(d,CH_3, $^3J_{CH(CH_3)_2}$ 7.0Hz)
$[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Br_3][BPh_4]$	CD_3NO_2	5.67(H_AH_B 17Hz; J 6.0Hz) 2.86(sp $C\underline{H}Me_2$) 2.25(s,CH_3) 1.31(d,CH_3 of $CHMe_2$ J 7.0Hz)	
$[OsRu(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ (e)	CD_3NO_2	6.01(s,C_6H_6-Os) 5.43(s, C_6H_6-Ru)	4.47(s, OMe)
$[Ru(\eta\text{-}C_6H_6)_2][BF_4]_2$	$(CD_3)_2SO$	6.89(s)	
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)][BF_4]_2$	$(CD_3)_2SO$	6.86(s,C_6H_6) 6.93(s,$C_6\underline{H}_3Me_3$) 2.37(s,$C_6H_3\underline{Me}_3$)	

Table 2.2 (contd.)

(a) Reference standard-internal TMS lock

(b) Where appropriate $[BPh_4]^-$ resonances observed between δ6.8 - 7.5 ppm

(c) Proton resonance from hydroxyl group not observed

(d) Partially masked by $[BPh_4]^-$ resonances

(e) NMR parameters determined from the spectrum of a mixture

Table 2.3 Fractional coordinates for $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$

Atom Cation	X	Y	Z
Ru(1)	0.15343(20)	0.08120(24)	0.63243(6)
Ru(2)	0.36205(20)	0.09326(25)	0.61283(6)
Ru(3)	0.30022(19)	0.32968(22)	0.66051(5)
Ru(4)	0.20143(19)	0.33461(22)	0.59124(5)
O(1)	0.2953(16)	0.0290(16)	0.6516(4)
O(2)	0.2168(15)	0.0391(16)	0.5906(4)
O(3)	0.3416(15)	0.3867(17)	0.6174(4)
O(4)	0.1622(15)	0.3779(17)	0.6349(4)
O(5)	0.2558(16)	0.2093(11)	0.6256(4)
C(1)	0.2606(24)	0.347(3)	0.7075(7)
C(2)	0.300(3)	0.2448(25)	0.7048(9)
C(3)	0.391(3)	0.2312(25)	0.6968(8)
C(4)	0.4477(25)	0.310(3)	0.6905(7)
C(5)	0.413(3)	0.418(3)	0.6913(8)
C(6)	0.319(3)	0.422(3)	0.7011(9)
C(7)	0.494(3)	0.197(3)	0.6121(9)
C(8)	0.455(3)	0.180(3)	0.5828(9)
C(9)	0.4362(25)	0.082(3)	0.5698(7)
C(10)	0.454(3)	-0.014(3)	0.5879(8)
C(11)	0.500(3)	-0.001(3)	0.6205(8)
C(12)	0.518(3)	0.110(3)	0.6339(8)
C(13)	0.080(3)	0.053(3)	0.6751(8)
C(14)	0.058(3)	0.160(3)	0.6650(8)
C(15)	0.0053(21)	0.1753(24)	0.6308(6)
C(16)	-0.0088(22)	0.083(3)	0.6121(7)
C(17)	0.012(3)	-0.022(3)	0.6188(9)
C(18)	0.066(3)	-0.040(3)	0.6531(9)
C(19)	0.053(3)	0.332(3)	0.5628(8)
C(20)	0.0924(25)	0.436(3)	0.5624(7)
C(21)	0.1833(25)	0.460(3)	0.5527(7)
C(22)	0.2437(23)	0.3756(24)	0.5444(7)
C(23)	0.214(3)	0.2650(24)	0.5429(8)
C(24)	0.108(3)	0.244(3)	0.5539(9)

Table 2.3 (contd.)

	X	Y	Z
Acetone Solvent Molecules			
O(6)	0.5597(18)	0.4045(23)	0.3861(5)
O(7)	-0.0574(16)	0.4207(20)	0.3615(5)
C(73)	0.076(3)	0.315(3)	0.3442(8)
C(74)	0.0122(24)	0.412(3)	0.3448(7)
C(75)	0.023(3)	0.507(3)	0.3222(8)
C(76)	0.481(3)	0.493(3)	0.4261(8)
C(77)	0.4946(24)	0.400(3)	0.4040(7)
C(78)	0.420(3)	0.304(3)	0.4013(9)
Tetraphenylborate A			
B(1)	0.225(3)	0.730(3)	0.2638(8)
C(25)	0.2801(18)	0.7338(18)	0.2288(4)
C(26)	0.2171(18)	0.7634(18)	0.2006(4)
C(27)	0.2572(18)	0.7720(18)	0.1716(4)
C(28)	0.3602(18)	0.7511(18)	0.1710(4)
C(29)	0.4232(18)	0.7215(18)	0.1992(4)
C(30)	0.3831(18)	0.7128(18)	0.2282(4)
C(31)	0.2780(14)	0.6168(11)	0.2842(4)
C(32)	0.2962(14)	0.5232(11)	0.2668(4)
C(33)	0.3294(14)	0.4274(11)	0.2832(4)
C(34)	0.3445(14)	0.4253(11)	0.3168(4)
C(35)	0.3263(14)	0.5190(11)	0.3342(4)
C(36)	0.2931(14)	0.6147(11)	0.3178(4)
C(37)	0.2604(16)	0.8394(15)	0.2863(4)
C(38)	0.3250(16)	0.9191(15)	0.2766(4)
C(39)	0.3377(16)	1.0184(15)	0.2931(4)
C(40)	0.2859(16)	1.0381(15)	0.3193(4)
C(41)	0.2214(16)	0.9585(15)	0.3290(4)
C(42)	0.2087(16)	0.8591(15)	0.3125(4)
C(43)	0.0997(11)	0.7189(17)	0.2542(4)
C(44)	0.0549(11)	0.6187(17)	0.2445(4)
C(45)	-0.0498(11)	0.6127(17)	0.2343(4)
C(46)	-0.1096(11)	0.7067(17)	0.2337(4)
C(47)	-0.0648(11)	0.8068(17)	0.2433(4)
C(48)	0.0399(11)	0.8129(17)	0.2535(4)

Table 2.3 (contd.)

	X	Y	Z
Tetraphenylborate B			
B(2)	0.258(3)	0.771(3)	0.4824(8)
C(49)	0.3923(11)	0.7645(16)	0.4921(5)
C(50)	0.4468(11)	0.8571(16)	0.5039(5)
C(51)	0.5514(11)	0.8501(16)	0.5141(5)
C(52)	0.6016(11)	0.7504(16)	0.5124(5)
C(53)	0.5471(11)	0.6578(16)	0.5006(5)
C(54)	0.4425(11)	0.6648(16)	0.4905(5)
C(55)	0.2235(14)	0.6677(14)	0.4594(4)
C(56)	0.2102(14)	0.5668(14)	0.4738(4)
C(57)	0.1842(14)	0.4749(14)	0.4546(4)
C(58)	0.1716(14)	0.4840(14)	0.4210(4)
C(59)	0.1849(14)	0.5849(14)	0.4067(4)
C(60)	0.2108(14)	0.6768(14)	0.4258(4)
C(61)	0.2326(15)	0.8929(13)	0.4675(4)
C(62)	0.2785(15)	0.9279(13)	0.4413(4)
C(63)	0.2522(15)	1.0288(13)	0.4269(4)
C(64)	0.1802(15)	1.0948(13)	0.4388(4)
C(65)	0.1344(15)	1.0599(13)	0.4650(4)
C(66)	0.1606(15)	0.9589(13)	0.4793(4)
C(67)	0.2139(15)	0.7583(14)	0.5177(4)
C(68)	0.1094(15)	0.7401(14)	0.5155(4)
C(69)	0.0642(15)	0.7301(14)	0.5435(4)
C(70)	0.1237(15)	0.7383(14)	0.5737(4)
C(71)	0.2283(15)	0.7565(14)	0.5759(4)
C(72)	0.2734(15)	0.7665(14)	0.5479(4)

Table 2.4 Selected bond distances and angles for the cation $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)]^{2+}$

(a) Bond lengths (Å) with standard deviations ( )

Ru(1)-Ru(2)	3.001(21)	Ru(2)-O(1)	2.110(19)
Ru(1)-Ru(3)	3.708(25)	Ru(2)-O(2)	2.123(19)
Ru(1)-Ru(4)	3.646(25)	Ru(2)-O(5)	2.121(18)
Ru(2)-Ru(3)	3.672(25)	Ru(3)-O(3)	2.080(19)
Ru(2)-Ru(4)	3.676(25)	Ru(3)-O(4)	2.072(20)
Ru(3)-Ru(4)	3.007(21)	Ru(3)-O(5)	2.100(18)
Ru(1)-O(1)	2.040(19)	Ru(4)-O(3)	2.116(19)
Ru(1)-O(2)	2.112(19)	Ru(4)-O(4)	2.041(20)
Ru(1)-O(5)	2.119(18)	Ru(4)-O(5)	2.153(18)

(b) Bond angles (°) with standard deviations ( )

Ru(1)-O(1)-Ru(2)	92.6(8)	Ru(3)-O(3)-Ru(4)	91.6(8)
Ru(1)-O(2)-Ru(2)	90.2(7)	Ru(3)-O(4)-Ru(4)	94.0(8)
Ru(1)-O(5)-Ru(2)	90.1(7)	Ru(3)-O(5)-Ru(4)	90.0(7)
O(1)-Ru(1)-O(2)	78.3(8)	O(3)-Ru(3)-O(4)	77.2(8)
O(1)-Ru(1)-O(5)	73.3(7)	O(3)-Ru(3)-O(5)	73.3(7)
O(2)-Ru(1)-O(5)	74.3(7)	O(4)-Ru(3)-O(5)	72.5(7)
O(1)-Ru(2)-O(2)	76.5(7)	O(3)-Ru(4)-O(4)	77.1(8)
O(1)-Ru(2)-O(5)	71.8(7)	O(3)-Ru(4)-O(5)	71.5(7)
O(2)-Ru(2)-O(5)	74.0(7)	O(4)-Ru(4)-O(5)	72.0(7)
Ru(1)-O(5)-Ru(3)	123.0(9)	Ru(2)-O(5)-Ru(3)	120.9(9)
Ru(1)-O(5)-Ru(4)	117.2(8)	Ru(2)-O(5)-Ru(4)	118.6(8)

Table 2.5 Fractional coordinates[(a)] for $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2.12H_2O$

Atom	X	Y	Z
Ru	1558	1558	1558
O(1)	3241	3241	3241
C(1)	-2	803	1608
C(2)	338	338	1733
C(3)	1268	1268	-127
S	5092	5092	5092
O(2)	4405	4405	4405
O(3)	5783	5783	5783
$H_2O(1)$	0	2500	7500
$H_2O(2)$	1438	1438	7104
$H_2O(3)$	2500	2500	7500

(a) $\times 10^4$

Table 2.6 Fractional coordinates for $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4].MeOH$

Atom	X	Y	Z
Cation A			
Ru(1)	0.55840(4)	0.50000	0.49350(7)
Cl(3)	0.50000	0.3192(7)	0.50000
Cl(4)	0.5266(2)	0.5901(8)	0.5972(4)
C(7)	0.6666(7)	0.5893(19)	0.6667(7)
C(8)	0.5631(6)	0.4211(17)	0.3064(7)
C(9)	0.5337(9)	0.2829(19)	0.2904(15)
C(10)	0.6042(10)	0.4320(34)	0.2645(17)
C(1)	0.6354(4)	0.4014(7)	0.5520(4)
C(2)	0.6112(4)	0.3616(7)	0.4664(4)
C(3)	0.5930(4)	0.4605(7)	0.4021(4)
C(4)	0.5990(4)	0.5992(7)	0.4234(4)
C(5)	0.6232(4)	0.6391(7)	0.5090(4)
C(6)	0.6414(4)	0.5401(7)	0.5733(4)
Cation B			
Ru(2)	0.06102(5)	0.4476(2)	0.50422(9)
Cl(1)	0.0210(2)	0.5395(7)	0.5987(3)
Cl(2)	0.00000	0.2614(8)	0.50000
C(17)	0.1542(9)	0.5195(28)	0.6901(9)
C(18)	0.0855(9)	0.3289(23)	0.3372(11)
C(19)	0.0383(10)	0.2282(30)	0.3065(18)
C(20)	0.0695(12)	0.4444(31)	0.2706(18)
C(11)	0.1339(5)	0.3430(10)	0.5731(6)
C(12)	0.1406(5)	0.4811(10)	0.5958(6)
C(13)	0.1290(5)	0.5814(10)	0.5325(6)
C(14)	0.1107(5)	0.5435(10)	0.4464(6)
C(15)	0.1040(5)	0.4054(10)	0.4237(6)
C(16)	0.1156(5)	0.3051(10)	0.4870(6)

Table 2.6 (contd.)

Tetraphenylborate			
B(1)	0.2589(6)	0.0085(21)	0.4857(9)
C(21)	0.2149(3)	-0.0709(11)	0.4030(6)
C(22)	0.1616(3)	-0.0380(11)	0.3812(6)
C(23)	0.1223(3)	-0.1079(11)	0.3149(6)
C(24)	0.1363(3)	-0.2106(11)	0.2703(6)
C(25)	0.1896(3)	-0.2434(11)	0.2920(6)
C(26)	0.2289(3)	-0.1736(11)	0.3584(6)
C(27)	0.3219(3)	-0.0023(14)	0.4946(6)
C(28)	0.3332(3)	0.0129(14)	0.4214(6)
C(29)	0.3858(3)	0.0123(14)	0.4283(6)
C(30)	0.4270(3)	-0.0034(14)	0.5083(6)
C(31)	0.4157(3)	-0.0186(14)	0.5814(6)
C(32)	0.3631(3)	-0.0181(14)	0.5746(6)
C(33)	0.2608(4)	0.1836(8)	0.4790(6)
C(34)	0.2301(4)	0.2443(8)	0.3981(6)
C(35)	0.2258(4)	0.3865(8)	0.3906(6)
C(36)	0.2421(4)	0.4679(8)	0.4640(6)
C(37)	0.2628(4)	0.4072(8)	0.5449(6)
C(38)	0.2671(4)	0.2651(8)	0.5524(6)
C(39)	0.2491(4)	-0.0572(11)	0.5686(6)
C(40)	0.2173(4)	0.0081(11)	0.6047(6)
C(41)	0.2075(4)	-0.0543(11)	0.6714(6)
C(42)	0.2296(4)	-0.1821(11)	0.7019(6)
C(43)	0.2614(4)	-0.2474(11)	0.6658(6)
C(44)	0.2711(4)	-0.1849(11)	0.5991(6)
Methanol Solvate			
C(45)	0.5656(8)	0.4294(26)	0.0328(12)
C(46)	0.5301(8)	0.4143(26)	-0.0492(11)

Table 2.7 Bond lengths and angles for $[Ru_2(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)_2Cl_3][BPh_4].MeOH$

(a) Bond lengths (Å) with standard deviation ( )

Cation B		Cation A	
Ru(2)-Ru(2')	3.282(3)	Ru(1)-Ru(1')	3.283(3)
Ru(2)-Cl(1)	2.431(7)	Ru(1)-Cl(3)	2.411(5)
Ru(2)-Cl(2)	2.449(6)	Ru(1)-Cl(4)	2.406(7)
Ru(2)-C(11)	2.139(11)	Ru(1)-Cl(1)	2.174(8)
Ru(2)-C(12)	2.153(11)	Ru(1)-C(2)	2.152(9)
Ru(2)-C(13)	2.168(12)	Ru(1)-C(3)	2.137(10)
Ru(2)-C(14)	2.169(14)	Ru(1)-C(4)	2.144(10)
Ru(2)-C(15)	2.155(14)	Ru(1)-C(5)	2.166(9)
Ru(2)-C(16)	2.141(13)	Ru(1)-C(6)	2.180(8)

Tetraphenylborate

B(1)-C(21)	1.644(17)
B(1)-C(27)	1.673(19)
B(1)-C(33)	1.722(22)
B(1)-C(39)	1.656(21)

(b) Bond Angles (°) with standard deviations

Cation B		Cation A	
Ru(2)-Cl(1)-Ru(2')	82.21(20)	Ru(1)-Cl(3)-Ru(1')	85.84(13)
Ru(2)-Cl(2)-Ru(2')	84.13(15)	Ru(1)-Cl(4)-Ru(1')	86.15(22)
Cl(1)-Ru(2)-Cl(1')	79.01(20)	Cl(3)-Ru(1)-Cl(4)	78.60(18)
Cl(1)-Ru(2)-Cl(2)	79.57(18)	Cl(3)-Ru(1)-Cl(4')	78.68(18)
Cl(1')-Ru(2)-Cl(2)	79.84(18)	Cl(4)-Ru(1)-Cl(4')	78.42(22)

CHAPTER 3

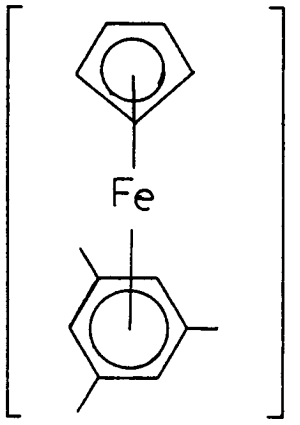
The Preparation, Characterisation and some Properties of Ruthenium(II) and Osmium(II) Mixed Sandwich Complexes

3.1 Introduction

The first synthesis of a transition metal sandwich complex containing both a η^5-cyclopentadienyl and an aromatic ligand was reported by Coffield et al in 1957[108]. This area of transition metal chemistry however remained largely unexplored until Nesmeyanov et al observed that η-arene η-cyclopentadienyl iron cations were readily prepared by the Lewis acid catalysed cleavage of ferrocene in the presence of an aromatic substrate[109,110]. Since that time a large body of literature has developed pertaining to these systems[111]. However to date there have been few reports of the synthesis of the analogous ruthenium(II) and osmium(II) cations. In this chapter an extension of the first high yield synthesis[112] of these structural analogues is reported, together with the results of investigations into the physical and chemical properties of these species. Firstly, however it is useful to briefly survey the synthesis and physio-chemical properties of the iron complexes, so that useful comparisons may be made.

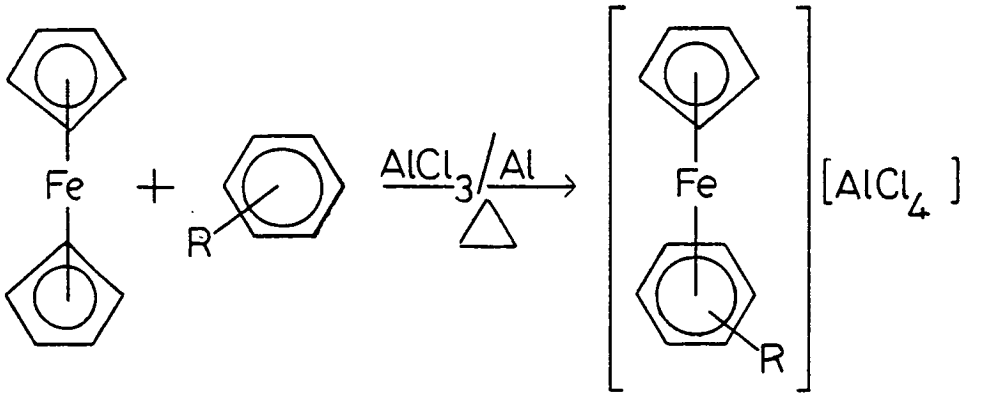
The initial report of the preparation of $[Fe(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta\text{-}C_5H_5)]I$ (Equation [9]) by reaction of $[Fe(\eta\text{-}C_5H_5)(CO)_2]Cl$ with mesitylene in the presence of aluminium chloride was followed by a patent[113] in which the extension of the reaction to the ruthenium and osmium analogues was reported.

$$[Fe(\eta\text{-}C_5H_5)(CO)_2]Cl \xrightarrow[AlCl_3]{1,3,5\text{-}C_6H_3Me_3} \text{and then} \xrightarrow{H_2O/KI}$$



I ...[9]

In 1960 Wilkinson et al[114] reported the preparation of the iron η-benzene complex, which was isolated as its tribromide. However it was Nesmeyanov et al who first reported the most useful general synthetic route to these cations[109,110] (Equation [10]). In a typical reaction the reagent ratios of ferrocene:$AlCl_3$:Al:arene used are 1:2:1:excess, and the aromatic substrate is used as the solvent. In the case of solid arenes the reaction can either be carried out as a melt[115], or in some inert hydrocarbon solvent[116-118]. The presence of aluminium powder in the reaction mixture prevents any oxidation of ferrocene to the ferricinium cation. The mixed sandwich iron cations have been isolated as a variety of salts[111].



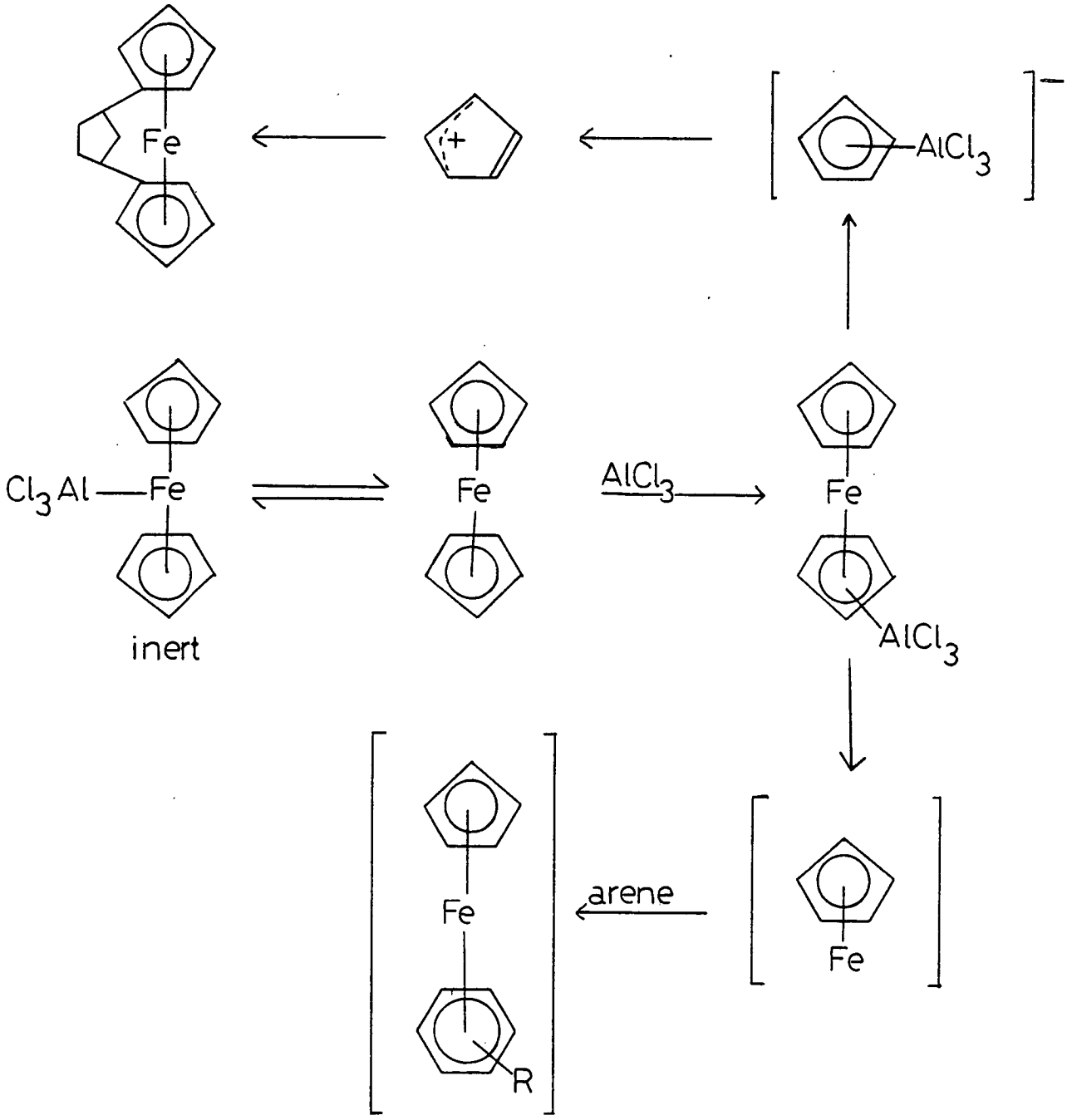
.....[10]

This synthetic route can be readily extended to 1,1'-dialkylferrocenes, though the 1,1'-diacetylferrocenes are relatively inert[116]. Additionally, the reaction with acetylferrocene leads to complexes containing a substituted cyclopentadienyl ring and/or dications of the type $[Fe(\eta\text{-arene})_2]^{2+}$ [119,120].

Extensive studies on the mechanisms[111] of these processes has shown that successful reaction proceeds *via* complexation of $AlCl_3$ to the electron rich cyclopentadienyl ring, weakening the metal-carbon bond which can then break either unimolecularly to form an essentially free $[Fe(\eta\text{-}C_5H_5)]^+$ unit and a cyclopentadienyl anion or undergoes nucleophilic attack by an aromatic substrate to form an η-arene η-cyclopentadienyl iron cation directly. The cyclopentadienide anion would, after protonation, alkylate ferrocene to form cyclopentylferrocenes[121] which have been isolated from the organic phase of the ligand exchange reactions[122]. The 1,1'-diacylferrocenes react with two moles of $AlCl_3$ at the carbonyl groups to

form bis α-ferrocenyl carbenium ions which are unstable and decompose to give complex products[120]. The reaction mechanism is summarised in Scheme 3.1.

Scheme 3.1 A mechanism for the reaction of ferrocene with aromatic substrates in the presence of the Lewis Acid $AlCl_3$



The $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations have been shown to be susceptible to nucleophilic attack by hydride ion, to form neutral η^5-cyclohexadienyl, η^5-cyclopentadienyl iron complexes[123,124]. Studies on the complexes containing substituted benzenes have shown that the position of attack depends on the nature of the substituents[115,125,126]. Thus if the benzene has methyl substituents, the incoming hydride ion added to the unsubstituted arene carbon whereas the hydride preferred to attack ortho to a halogen substituent, and a complex mixture of η^5-cyclohexadienyl products was obtained upon reaction with η-methoxyarenes. Nucleophilic attack by sodamide, sodium ethoxide or sodium hydroxide on the $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cation leads to disproportionation to form ferrocene, benzene and Fe(II) ions[127]. These complexes have also been shown to react with a variety of organometallic reagents to give the 6-exo products analogous to those obtained by reaction with hydride ion[128,129]. Directive effects similar to those observed for the hydride reactions have been noted[115,125,126]. This rich chemistry of the iron complexes is in contrast to that of the ruthenium and osmium anologues discussed later.

Several electrochemical investigations have been carried out on these $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations[130-133]. These studies have shown that the cations undergo a one-electron reversible reduction, at between -1.2 and -1.8 V (vs. Ag/AgI) and a further irreversible reduction at more negative potential. The first step involves reduction to a neutral radical[131,132] and the second its conversion to a cyclohexadienyl complex[132] (Equation [11]).

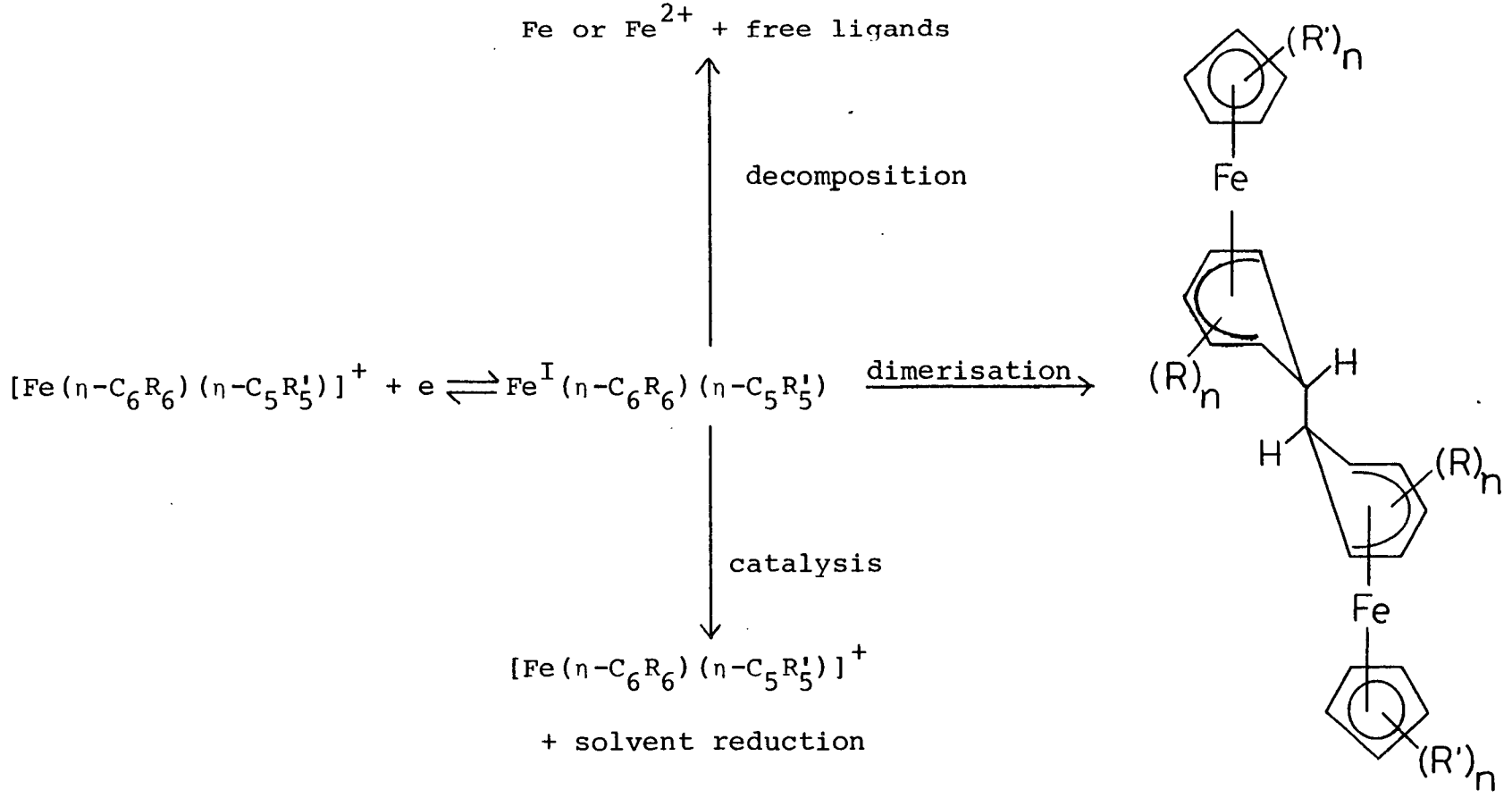
$$[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+ + e \rightleftharpoons Fe^{I}(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)$$

$$Fe^{I}(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5) + e + H^+ \longrightarrow Fe(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5) \quad \ldots[11]$$

Subsequent studies[134-136] in basic aqueous and alcoholic media have shown that the behaviour of these radicals (Scheme 3.2) depends on the nature and on the number of substituents on the rings and also on the medium.

Finally these iron cations were found to be photochemically active but the initial report[110] noted that light accelerated the decomposition of the cations. A later study[137] found that ferrocene was formed when any of the cations were irradiated by light of wavelength 253-577 mμ. Mann and Gill[47] have recently utilised this observation to synthesise complexes, $[Fe(\eta\text{-}C_5H_5)L_3]X$ (L_3 = C_6Me_6, triphos, $(CO)_3$ <u>etc</u>.; X = BF_4, PF_6) from $[Fe(\eta\text{-}1,4\text{-}C_6H_4Me_2)(\eta\text{-}C_5H_5)]X$ by photochemical reaction with an excess of the ligand in methylene chloride or acetone.

Scheme 3.2 The Electrochemical behaviour of the cation $[Fe(\eta\text{-}C_6R_n)(\eta\text{-}C_5R'_n)]^+$



3.2 Results and Discussion

In contrast to the large volume of literature on the iron(II) complexes there have been few papers published on the synthesis and reactions of their ruthenium and osmium anologues. As mentioned previously Coffield reported the synthesis of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru, Os) via reaction of $[M(\eta\text{-}C_5H_5)(CO)_2]^+$ cations with the appropriate arene[113], Zelonka and Baird have reported that $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ reacts with $Tl[C_5H_5]$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$[25] and there have been two reports[138,139] of the synthesis of the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations by the Nesmeyanov route described above (see Scheme 3.3). Unfortunately using ruthenocene the latter method requires long reaction times, high temperatures and only low yields are obtained (<10%)[138]. These yields can be increased to 30% (for arene = $1,3,5\text{-}C_6H_3Me_3$) by addition of water to the reaction mixture but with C_6Me_6 this also results in extensive demethylation and disproportionation of the aromatic ligand[139].

Scheme 3.3 The synthesis of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations from ruthenocene

$$Ru(\eta\text{-}C_5H_5)_2 + \text{arene} \xrightarrow[NaX]{AlHal_3/Al} [Ru(\eta\text{-arene})(\eta\text{-}C_5H_5)]X + (C_5H_5)_n$$

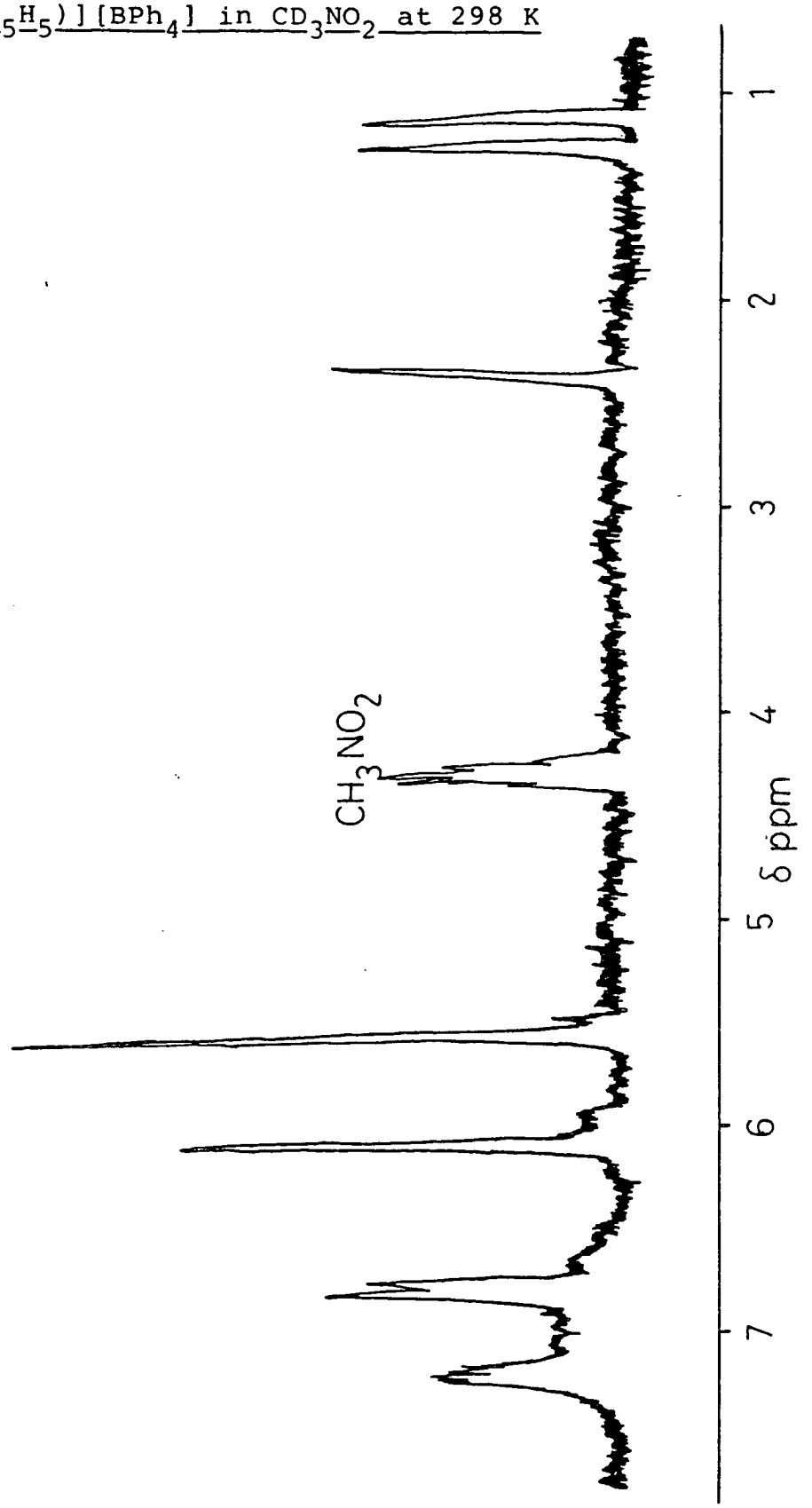
(Arene = C_6H_6, $C_6H_5CH_3$, $C_6H_5C_6H_5$, C_6H_5Cl;
X^- = BF_4, PF_6, BPh_4; hal = Cl, Br)

$Ru(\eta\text{-}C_5H_5)_2$:$AlHal_3$:Al:Arene = 1:3-5:1:excess

The complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ reported by Zelonka and Baird was prepared in high yield by reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with $Tl[C_5H_5]$ in acetonitrile at ambient temperature. The reactions of a wide range of $[Ru(\eta\text{-arene})Cl_2]_2$ (arene = C_6H_6, 1,4-$MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6) with $Tl[C_5H_5]$ have now been investigated, together with their extension to some of the analogous osmium complexes.

Thus, reaction of $[M(\eta\text{-arene})Cl_2]_2$ with $Tl[C_5H_5]$ (1:2 molar ratio) in acetonitrile for several hours at ambient temperature gave a fine precipitate of TlCl which was removed by filtering through celite. Removal of the solvent and subsequent treatment of the residual solid or oil with a methanolic solution of $Na[BPh_4]$ produced the desired $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)][BPh_4]$ as a greyish-white or pale brown solid. The infrared spectrum of the products did not contain any bond assignable to either bridging or terminal ν(M-Cl) vibrations. However bands at ca. 840 cm^{-1} and ca. 600 cm^{-1} were indicative of a π-bonded arene, while bands at ca. 760, 1100 and 1400 cm^{-1} could be assigned to the π-bonded cyclopentadienyl (cf. bands in the parent iron cation at 780, 853, 1006, 1112 and 1419 cm^{-1} assigned to the cyclopentadienyl ring[140]). Conductivity measurements were consistent with a 1:1 electrolyte. The ^1H n.m.r. spectrum of a typical complex (Figure 3.1) contains a singlet at ca. 5.0-5.6 ppm which

Figure 3.1 The ^{1}H n.m.r. spectrum of $[Os(\eta\text{-}1,4\text{-}MeC_6H_4\text{-}CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ in CD_3NO_2 at 298 K



can be attributed to the π-bonded cyclopentadienyl ligand as well as typical resonances for the particular arene. In the reaction using $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$, treatment of the residue with a methanolic solution of $NH_4[PF_6]$ gave $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6]_2.NH_4PF_6$ (cf. $[Ru(\eta\text{-}C_6H_6)Cl(NH_3)_2]_3[PF_6]_3.NH_4PF_6$)[11]. For M = Ru, yields of 50-80% were obtained, a substantial improvement upon those reported for the other synthetic routes while for M = Os, lower yields of 20-40% were realised. The lower yields obtained with the osmium complexes are a general feature of much of the chemistry of these η-arene species. The compounds were characterised by elemental analyses (Table 3.1), hydrogen-1 n.m.r. (Table 3.2) and carbon-13 n.m.r. (Table 3.3) spectroscopy and by conductivity measurements in $(CH_3)_2SO$ or CH_3NO_2 (see Experimental Section).

The cations $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ show distinct trends in both their hydrogen-1 and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra, as reported previously for the Fe and Ru analogues[138]. On descending the triad the position of the $\eta\text{-}C_5H_5$ protons shift to higher frequency, e.g. for the cations, $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$, M = Fe, δ5.23[138]; M = Ru, 5.43; M = Os, 5.67 ppm. Conversely, the benzene protons resonate at lower frequency on descending the triad e.g. for the $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cations, M = Fe, δ6.44[138]; M = Ru, δ6.20; M = Os, 6.14 ppm. In the $^{13}C\text{-}\{^1H\}$ spectra both $\eta\text{-}C_6H_6$ and $\eta\text{-}C_5H_5$ resonances are

shifted to lower frequency on descending the triad, although the benzene resonance is shifted to a greater extent than the cyclopentadienyl resonance, thus making the unequivocal assignment of the spectrum of $[Os(\eta-C_6H_6)(\eta-C_5H_5)][BPh_4]$ impossible. As suggested earlier[138], this might indicate that the positive charge of the cations is delocalised onto the arene ligand in the order Fe > Ru > Os.

3.3 Some attempted reactions of the $[M(\eta-arene)(\eta-C_5H_5)]^+$ cations (M = Ru, Os)

As discussed in the introduction, the iron(II) analogues of these cations are very susceptible to nucleophilic attack on the coordinated arene rings, to give stable substituted cyclohexadienyl complexes. The isoelectronic $[Rh(\eta-C_5Me_4Et)(\eta-C_6H_6)]^{2+}$ [141] cation readily undergoes similar reactions and several other ruthenium(II) arene cations have recently been shown to undergo nucleophilic attack to give stable η^5-cyclohexadienyl complexes[13,19].

If however the positive charge of the cations is delocalised onto the arene ligand in the order Fe > Ru > Os then we might expect a decreased reactivity towards nucleophilic attack as we descend the triad. Our investigations into the reactions of some of the $[M(\eta-arene)(\eta-C_5H_5)]^+$ cations with various nucleophiles

(Y) gave either no reaction (M = Ru; Y = various PR_3; M = Os, Y = various PR_3, H^-, CN^-, OH^-) or extensive decomposition which probably involved displacement of both the carbocyclic rings (M = Ru, Y = CN^-, OH^-). However evidence has been found for nucleophilic attack on the arene ring on treatment of the $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cation with $Na[BH_4]$ [142] in 1,2-dimethoxyethane. This gave the neutral compound $Ru(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)$ in very low yield (ca. 5%). The compound was identified by its hydrogen-1 n.m.r. spectrum and mass spectral fragmentation pattern (Experimental section) which were both similar to those of $[Fe(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ [124,143].

A similar reduction of reactivity towards tertiary phosphines in the order Fe >> Ru > Os has been observed in the series $[M(\eta\text{-}C_6H_6)_2][PF_6]_2$, and this has been attributed to the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II} [144].

The influence of ultra-violet radiation on the iron(II) cations $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ has already been discussed. However, preliminary attempts to extend these reactions to the ruthenium(II) and osmium(II) analogues have to date been unsuccessful. Other workers have shown that p-cymene is often the most labile arene bound to ruthenium(II) centres in a variety of systems [5]. However irradiation of $[M(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ (M = Ru, Os) in CH_2Cl_2 or CH_3NO_2 in the presence of an excess of the potential ligands

(hexamethylbenzene, dimethylphenylphosphine, or triphenylphosphine) gave only unreacted starting material, upon work-up of the reaction mixture, after 3-4 hours irradiation. However an investigation of the photochemistry of $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][PF_6]$ in acetonitrile has led to the isolation of the synthetically useful salt $[Ru(\eta\text{-}C_5H_5)(CH_3CN)_3][PF_6]$ [46].

Finally, in view of the extensive studies on the electroreduction of various $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations an electrochemical study was carried out on the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)][BPh_4]$ complexes. However, unlike the iron compounds, cyclic voltammetric and A.C. polarographic studies in CH_3NO_2 and CH_3CN showed that all the ruthenium and osmium mixed sandwich compounds studied (see Experimental section) resisted reduction upto the solvent limit. The complexes $[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$, $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)][BPh_4]$ and $[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ did undergo oxidation at fairly modest potentials, unlike $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][PF_6]$ which shows no oxidation wave upto the solvent limit, but unfortunately these processes remained irreversible in nature even at low temperatures (233 K) and high scan rates (100 Vs^{-1}). It seems highly likely that the irreversible wave can be attributed to the oxidation of the $[BPh_4]^-$ anion, since the complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6]_2.NH_4PF_6$ is redox inactive.

It is likely that these disappointing electrochemical observations can also be correlated with the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II}.

3.4 Experimental

Microanalyses, infrared and n.m.r. spectra, melting point and conductivity measurements were obtained as described in previous chapters. Mass spectra were measured on an A.E.I. MS9 spectrometer. Electrochemical studies were carried out using a Princeton Applied Research (PAR 170) electrochemistry system (potentiostat and programmer) employing a three-electrode cell configuration. All solutions were degassed with solvent saturated argon prior to measurement. The electrolyte solution was tetrabutylammonium tetrafluoroborate ($TBABF_4$) in either CH_2Cl_2, CH_3CN or CH_3NO_2 with Pt working and auxilliary electrodes and a Ag/AgI reference electrode (with respect to this reference electrode, ferrocene is oxidised at +0.60 V).

Materials

As in Chapter 1 together with thallium(I) cyclopentadienide which was prepared from freshly cracked cyclopentadiene and thallium(I) sulphate[145].

Microanalytical data are presented in Table 3.1, while hydrogen-1-n.m.r. and carbon-13-n.m.r. data are given in Tables 3.2 and 3.3 respectively.

Bis[η-Benzene-η-cyclopentadienylruthenium(II)hexafluorophosphate](2/1)-ammoniumhexafluorophosphate

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.30 g; 0.60 mmol) was dissolved in acetonitrile (80 ml) and $Tl[C_5H_5]$ (0.32 g; 1.17 mmol) was added. The reaction mixture was stirred under nitrogen for four hours. The precipitated thallium(I)chloride was removed by filtration through celite. The resulting orange solution was evaporated to dryness on a rotary evaporator and the orange-brown residue redissolved in a small amount of methanol (3 ml). Addition of an excess of $NH_4[PF_6]$ precipitated a light brown solid mp 110-112°C (yield 280 mg; 60%). Λ_m (10^{-3} mol dm^{-3} in $(CH_3)_2SO$ at 303 K) = 40 S cm^2 mol^{-1}.

η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienylruthenium(II)tetraphenylborate

The compound $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.30 g; 0.49 mmol) was dissolved in acetonitrile (80 ml) and $Tl[C_5H_5]$ (0.29 g; 1.06 mmol) was added. The reaction mixture was stirred under nitrogen for two hours. The precipitated thallium(I) chloride was removed by filtration through celite and the resulting solution evaporated to dryness. The orange-brown residue was redissolved in methanol (3 ml) and an excess of $Na[BPh_4]$ (0.20 g; 0.58 mmol) added to produce a pale greyish-brown precipitate which was filtered off, washed with

methanol and diethylether and dried in vacuo at 56°C m.p. 168-169°C (decomp.) (yield 510 mg; 82%).

η-Methoxybenzene-η-cyclopentadienylruthenium(II)-tetraphenylborate m.p. 123-125°C (yield 260 mg; 47%), and η-hexamethylbenzene-η-cyclopentadienylruthenium(II)-tetraphenylborate m.p. 252°C (decomp.) (yield 150 mg; 64%), Λ_m (10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 51 S cm^2 mol^{-1} were also synthesised from the corresponding [Ru(η-arene)-Cl_2]$_2$ and Tl[C_5H_5] followed by treatment with Na[BPh_4]. An impure sample of [Ru(η-C_6Me_6)(η-C_5H_5)]Cl (contaminated with excess TlCl) was also characterised by ^1H and ^{13}C-{^1H} n.m.r. spectroscopy (see Tables 3.2 and 3.3).

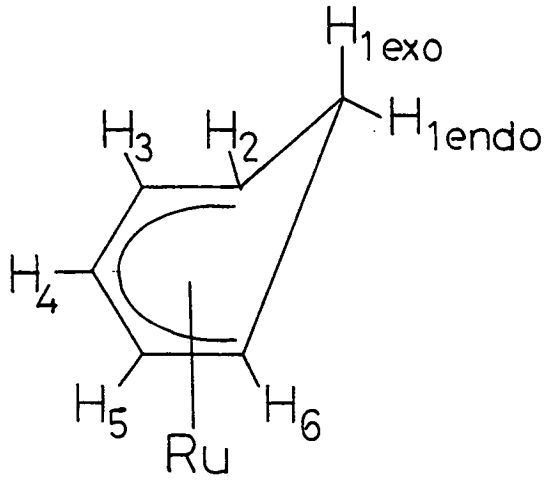
η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienyl-osmium(II)tetraphenylborate

The compound [{Os(η-p-$MeC_6H_4CHMe_2$)Cl_2}$_2$] (0.16 g; 0.20 mmol) was suspended in acetonitrile (50 ml) and Tl[C_5H_5] (0.22 g; 0.82 mmol) was added. The reaction mixture was stirred under nitrogen for two hours and then filtered through celite to remove thallium(I) chloride. Removal of solvent gave a yellowish oil which was dissolved in methanol (3 ml) and treated with Na[BPh_4] (0.20 g; 0.58 mmol) to give a greyish-white precipitate. This was filtered off, washed with methanol, chloroform and diethylether and dried in vacuo at 56°C m.p. 245°C (decomp.) (yield 120 mg; 43%) Λ_m(10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 48 S cm^2 mol^{-1}.

η-Benzene-η-cyclopentadienylosmium(II)tetraphenylborate m.p. 125-126°C (yield 120 mg; 17%) was similarly prepared from $[Os(\eta\text{-}C_6H_6)Cl_2]_2$, $Tl[C_5H_5]$ and $Na[BPh_4]$.

η^5-Cyclohexadienyl-η-cyclopentadienylruthenium(II)

The complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ (0.20 g; 0.72 mmol) was dissolved in 1,2-dimethoxyethane (50 ml) and $Na[BH_4]$ (0.24 g; 6.30 mmol) added in small amounts over a 20 minute period while the reaction mixture was stirred under nitrogen. After 4 hours, water was added to destroy the excess of $Na[BH_4]$ and the solvent removed under vacuo to give a dark brown residue. On shaking this with petroleum ether (b.p. 60-80°C) a very small amount of the product was extracted and removal of solvent gave a yellow solid (ca. 5% yield). ^1H n.m.r. in $CDCl_3$ at 301 K 5.79 (m) (H_4), 4.72 s ($\eta\text{-}C_5H_5$); 4.43 (m), ($H_{3,5}$); 2.55 (m) ($H_{2,6}$, H_1 exo and endo)



Mass spectrum m/e (based on ^{102}Ru peak) 245 ($[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$); 167 ($[Ru(\eta\text{-}C_5H_5)]^+$); 123 ($[Ru(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]^{2+}$). Trace amounts of this product were also obtained when $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$ was treated with $Na[BH_4]$ in various solvents (tetrahydrofuran, dioxane). No evidence however for even trace amounts of $[Os(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ was found on treatment of $[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]BPh_4$ with $Na[BH_4]$ in various solvents.

Similarly reaction of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations with other nucleophiles (Y) such as CN^-, OH^- and various PR_3 gave either no evidence for reaction (M = Ru; Y = PR_3; M = Os, Y = PR_3, CN^-, OH^-) or extensive decomposition involving displacement of both carbocyclic rings (M = Ru; Y = CN^-, OH^-).

Electrochemical Investigation

$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ in 0.25 M $TBABF_4/CH_3NO_2$; no cathodic response to -1.50 V; irreversible oxidation at $E_{\frac{1}{2}}$ + 0.58 V (100 mV s^{-1} scan rate even at -24°C: remains irreversible at 100 V s^{-1} scan rate in 0.10 M $TBABF_4/CH_3CN$ but moves to +0.80 V in this solvent.

$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$; in 0.10 M $TBABF_4/CH_3CN$; no cathodic response to -2.60 V at -40°C. Irreversible oxidation at $E_{\frac{1}{2}}$ = +0.94 V (even at -40°C and 100 V s^{-1} scan rate).

[Os(n-p-$MeC_6H_4CHMe_2$)(n-C_5H_5)]BPh_4 in 0.10 M $TBABF_4/CH_3CN$; no cathodic response on scanning to -2.60 V at -40°C. Irreversible oxidation at $E_{\frac{1}{2}}$ = +0.56 V (100 V s^{-1} scan rate). Remains irreversible at -40°C.

Table 3.1 Analytical data for the mixed sandwich complexes[a]

	%C	%H
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6]_2.NH_4PF_6$ [b]	29.3(28.1)	2.9(2.8)
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$	75.6(75.6)	6.5(6.5)
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)][BPh_4]$	72.1(74.8)	5.5(5.7)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)][BPh_4]$	75.8(76.0)	6.8(6.7)
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$	65.9(66.1)	5.5(5.6)
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][BPh_4]$	63.1(64.4)	4.5(4.8)

[a] Calculated values in parenthesis

[b] Nitrogen analysis 1.5(1.5)

Table 3.2 Hydrogen-1 n.m.r. data at 301 K in $(CD_3)_2SO$ for some $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru, Os)

Compound	δ (ppm) [a,b]	
	η-arene	$\eta\text{-}C_5H_5$
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6]_2.NH_4PF_6$	6.20(s)	5.43(s)
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ [c]	6.11 (s,4H) 2.22 (s,CH_3) 1.15 (d,CH_3 of $CHMe_2$, J 6.0 Hz)	5.31(s)
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)][BPh_4]$	5.80-6.50(m,5H) 3.67 (s,OMe)	5.34(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)][BPh_4]$ [d]	2.39(s)	4.96(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	2.33(s)	5.09(s)
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][BPh_4]$	6.14(s)	5.67(s)
$[Os(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ [c,d]	6.15(s,4H) 2.43(s,CH_3) 1.24(d,CH_3 of $CHMe_2$, J 6.0 Hz)	5.59(s)

[a] Reference standard-internal Me_4Si lock.

[b] Where appropriate $[BPh_4]^-$ multiplets observed between δ6.80-7.60 ppm

[c] $CHMe_2$ septet not observed due to low solubility of compound

[d] Measured in CD_3NO_2

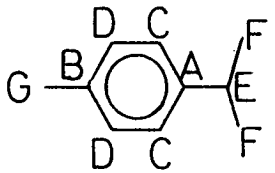
Table 3.3 Carbon-13 n.m.r. data (proton noise decoupled) at 301 K in $(CD_3)_2SO$ for some $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations

Compound	δppm [a,b]	
	η-arene	$\eta\text{-}C_5H_5$
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)_2][PF_6]_2.NH_4PF_6$	85.8	80.9
$[Ru(\eta\text{-}1,4\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)][BPh_4]$ [c]	111.7(A) 100.7(B) 86.0(C) 84.0(D) 31.2(E) 23.1(F) 19.6(G)	80.3
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)][BPh_4]$	(85.8, 84.1, 82.9, 80.0, 74.4)[d], 57.1[e]	79.6
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][BPh_4]$	76.1, 76.5[f]	
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	98.9[g], 17.3[h]	81.6

[a] Chemical shifts quoted to high frequency of $SiMe_4$ (internal lock)

[b] Where appropriate $[BPh_4]^-$ resonances observed between δ120-140 ppm.

[c] Labelling of p-cymene carbons



[d] Aromatic carbons of C_6H_5OMe

[e] Methyl carbon of C_6H_5OMe

[f] Not possible to assign resonances unambiguously as they are too close together and of similar intensity

[g] Aromatic carbons of C_6Me_6 [h] Methyl carbons of C_6Me_6

CHAPTER 4

The Synthesis, Properties and some Reactions of Osmium(III) Carboxylates

4.1 Introduction

A comprehensive review of the literature concerning metal-metal multiply bonded complexes has recently been published[146]. To place the new work on osmium(III)-carboxylates in context, a short introduction to related complexes of (a) molybdenum and tungsten, (b) rhodium and iridium, and (c) ruthenium and osmium, is presented here. The three groups have a common feature in that although many complexes containing the "$M_2(O_2CR)_4$" unit are now known for the 2nd row transition metals, there have been few reports to date of analogous 3rd row complexes. Before proceeding further it is of use to consider the bonding in a M-M multiple bond and why the carboxylate ligand is so important in this area of transition metal chemistry.

Bonding

The components of the M-M quadruple bond include the key elements in most other multiple bonds between pairs of metal atoms. Therefore the formation of a quadruple bond will be discussed first and then the modifications necessary for the formation of a bond of lower order considered.

Quadruple bonds are only found in transition metal chemistry since orbitals of angular momentum quantum number 2 (d orbitals) or higher (f, g *etc.*) are required. By considering only d orbitals a picture that is both qualitatively and even semiquantitatively correct can be obtained.

If the "M_2" unit is first considered in isolation, it is found that there are only five nonzero overlaps between pairs of d orbitals on the two atoms, (see Figure 4.1). The positive overlap of the two d_{z^2} atomic orbitals gives rise to σ bonding and σ^* antibonding molecular orbitals. The d_{xz} and d_{yz} overlaps can each give rise to a π bond; these two are equivalent but orthogonal, and hence constitute a degenerate orbital pair. These are also corresponding π^* antibonding orbitals resulting from negative overlap. Finally these are bonding molecular orbitals formed by overlap of the d_{xy} and $d_{x^2-y^2}$ orbitals, which form a degenerate pair of δ and δ^* bonds. Using the concept that MO energies are proportional to overlap integrals, then the ordering of the energy levels will be,

$$\sigma < \pi << \delta < \delta^* << \pi^* < \sigma^*$$

When a set of eight ligand atoms are introduced, (e.g. eight O atoms in $Mo_2(O_2CCH_3)_4$), then the symmetry is lowered and the degeneracy of the δ and δ^* orbitals removed. The $d_{x^2-y^2}$ orbitals now differ from the d_{xy} orbitals because the former now point approximately towards the ligands and the latter point between them, (or <u>vice versa</u> depending on how the coordinate axes are chosen). Thus one of the δ bonds inevitably becomes heavily involved in the metal-ligand σ bonds leaving only one pair of δ and δ^* orbitals for M-M bonding. An energy level diagram for M-M bonding is shown in Figure 4.2.

Figure 4.1 The five nonzero d-d overlaps between two metal atoms

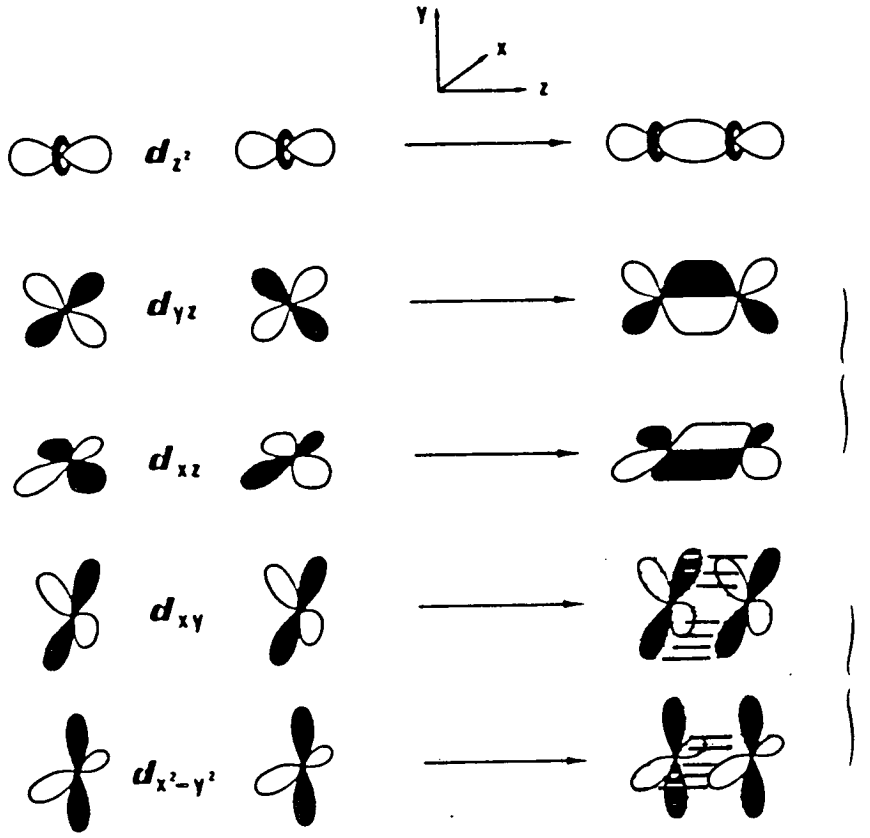
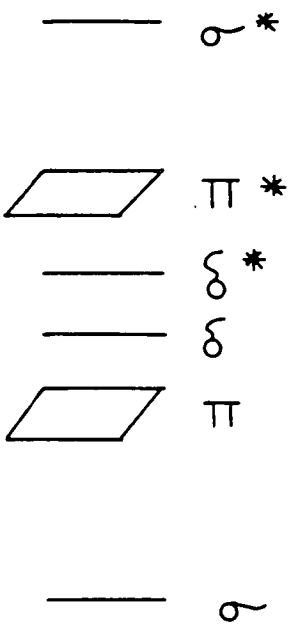


Figure 4.2 The qualitative ordering of the energy levels in a quadruple bond

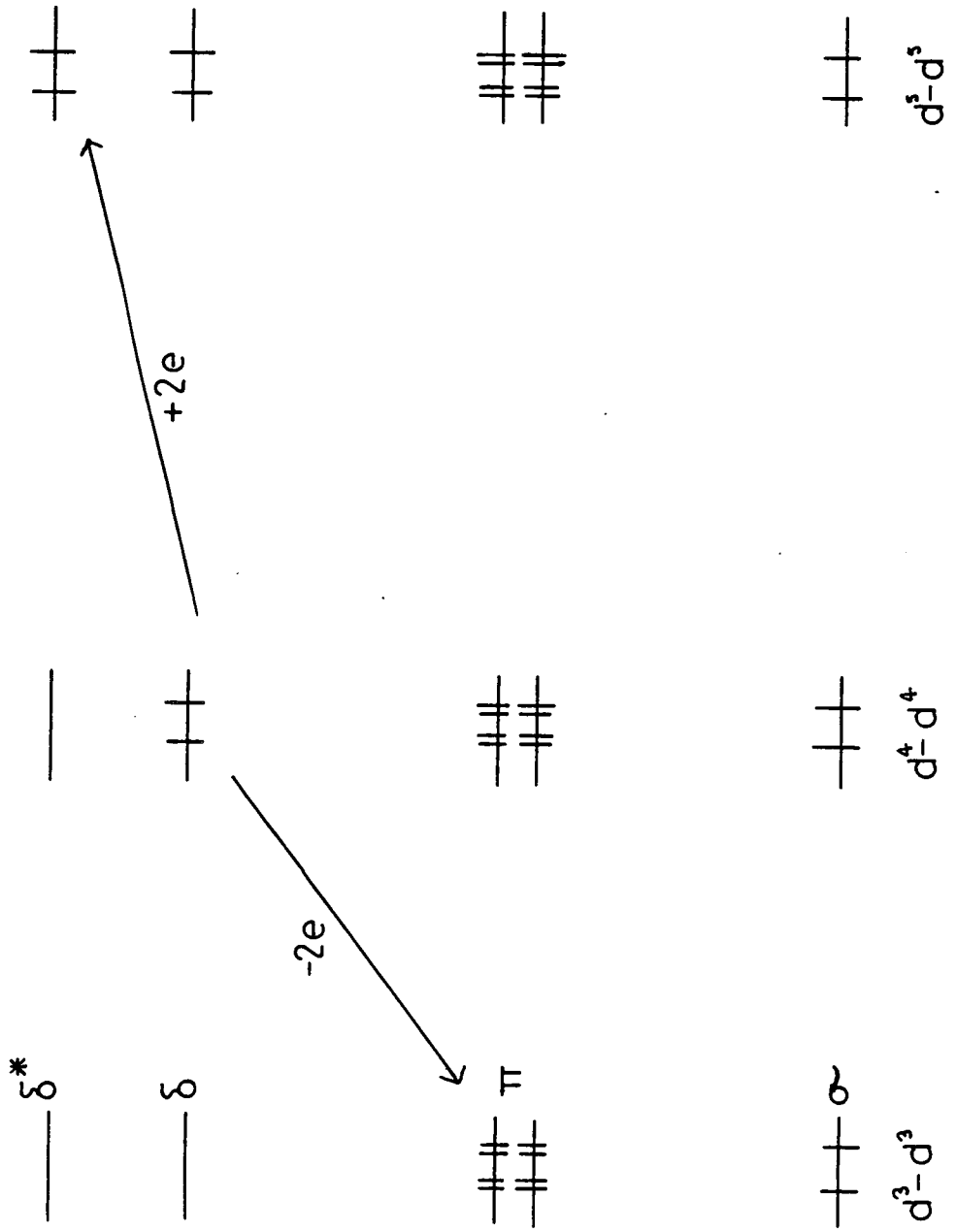


In the case of $Mo_2(O_2CR)_4$, there are eight valence electrons to be placed in these energy levels. These fill the four bonding molecular orbitals, producing the electronic configuration $\sigma^2\pi^4\delta^2$, and a bond order of 4. This is however, simply a statement of the net number of electron pairs that are binding together the two metal atoms. It does not provide a measure of bond strength except in the broadest qualitative sense. However the $\sigma^2\pi^4\delta^2$ description of the quadruple bond does account for the extreme shortness of these bonds and for the tendency of the ligands attached to the metals to be eclipsed (cf. the $[Re_2Cl_8]^{2-}$ ion).

There are two ways in which a quadruple bond may be modified to give a bond of lower order. Hence to obtain a triple bond two electrons may be removed from the orbital leaving a $\sigma^2\pi^4$ configuration, or less obviously, addition of two electrons to the δ^* orbital gives the configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ (see Figure 4.3). Examples containing both of these types of triple bond are known.

The gain or loss of a single electron from the $\sigma^2\pi^4\delta^2$ configuration to give a bond order of 3.5 is also possible (see Equation [12]). In fact up to four electrons may be added, leading to an electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ with a net bond order of 1.

Figure 4.3 The two modifications of the $\sigma^2\pi^4\delta^2$ configuration that gives triple bonds



Many dirhodium(II) species of the type $Rh_2(O_2CR)_4L_2$ contain single metal-metal bonds with this configuration.

$$[Mo_2Cl_8]^{4-} \longrightarrow [Mo_2(SO_4)_4]^{4-} + 8Cl^- \xrightarrow{O_2} [Mo_2(SO_4)_4]^{3-}$$

(B.O. 4) (B.O. 4) (B.O. 3.5)

..... [12]

The pervasiveness of the carboxylate ligand ($[RCO_2]^-$) in the chemistry of M-M multiply bonded complexes is attributed to the following features:

(1) The ligand readily coordinates in a bidentate fashion.

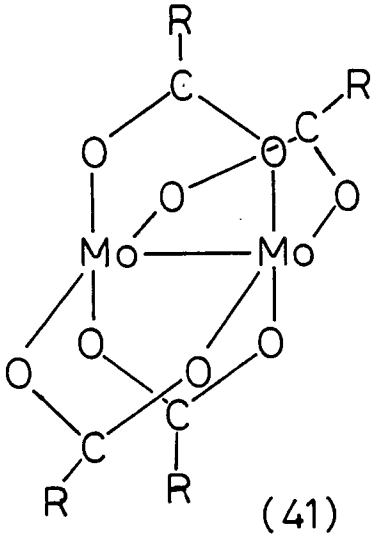
(2) The only conformation which the oxygen atoms can adopt is such that the lone pairs are directed along approximately parallel lines.

(3) The separation between oxygen atoms is of the same order of magnitude as a M-M multiple bond (2.0 - 2.5 Å).

Thus the carboxylate ligand is suitable for bridging the two metal centres and in so doing will impose a configuration in which the overlap of the δ orbitals is maximised. The ligand is also useful in that its properties can be varied in a variety of ways. Thus, its basicity can be altered by changing R from $C(CH_3)_3$ at one extreme to CF_3 at the other. Its steric properties can be changed from those with R=H to those with R=9-anthracenyl or 2-phenylphenyl. For these reasons the carboxylate ligand is probably one of the most important ligands in M-M multiply bonded complexes.

Molybdenum and Tungsten

The synthesis of the molybdenum(II) carboxylates, $Mo_2(O_2CR)_4$ (R = C_6H_5[147], CH_3[148], Et, Pr^n, Pr^i, C_6H_{11}, C_7H_{15}, C_3F_7, C_6H_4Me, C_6H_4OH, C_6H_4F[149]) was first reported, by Wilkinson et al, by reaction of molybdenum hexacarbonyl with the appropriate carboxylic acid, (and its anhydride if available), either alone or in diglyme. The X-ray structure analysis of $Mo_2(O_2CMe)_4$ (41) was published in 1965 by Lawton and Mason[150], and a subsequent more accurate re-determination[151] gave a Mo-Mo distance of 2.093(1) Å. An extensive range of these complexes is now available[146].



(41)

Interestingly, in the absence of a solvent such as diglyme then only a low yield of $Mo_2(O_2CMe)_4$ is found[152]. The main product is one or more of the trinuclear cations $[Mo_3X_2(O_2CMe)_6(H_2O)_3]^{n+}$, (X = either O or CCH_3 or one of each), where the Mo_3X_2 unit is a trigonal bipyramid in which the groups X occupy axial positions[153].

The structures of several other $Mo_2(O_2CR)_4$ compounds (R = H[154], CF_3[155], C_6H_5[156], CMe_3[156]) have been determined by X-ray crystallography and these confirm that the acetate structure is entirely typical and that coordination of axial ligands is not favoured here. Crystallographic studies on $Mo_2(O_2CPh)_4(diglyme)_2$[157] and $Mo_2(O_2CCF_3)_4(py)_2$[158] confirm that bonds to the axial ligands (2.663(6) and 2.548(8) Å respectively) are very long.

The heteronuclear compounds $CrMo(O_2CMe)_4$[159,160] and $MoW(O_2CMe_3)_4$[161,162] have also been prepared, the former by addition of $Mo(CO)_6$ to a refluxing solution of $Cr_2(O_2CMe)_4.2H_2O$ in acetic acid-acetic anhydride and the latter by refluxing a mixture of $Mo(CO)_6$ and $W(CO)_6$ (1:3 molar ratio) with pivalic acid in dichlorobenzene. Interestingly, crystal structure determinations of these compounds have shown that both the Mo-Cr and Mo-W distances (2.050(1) and 2.080(1) Å respectively) are shorter than the metal-metal distances in analogous dimolybdenum compounds.

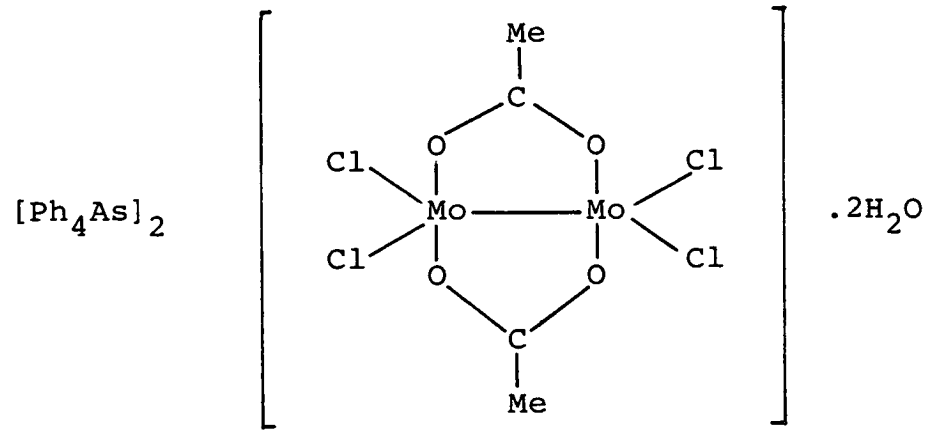
The compounds described above undergo three main types of chemical reaction: (a) reactions in which the "$Mo_2(O_2CR)_4$" unit is preserved: (b) reactions in which some or all of the carboxylate groups are displaced, but the Mo_2^{4+} core is retained, and (c) reactions leading to complete disruption of the dimer.

The reactions in which the $Mo_2(O_2CR)_4$ molecules remain intact are the formation of adducts of the type $Mo_2(O_2CR)_4L_2$ and one-electron oxidations to the $[Mo_2(O_2CR)_4]^+$ cations. The ability of molybdenum(II) carboxylates to form adducts was first noted by Wilkinson *et al*[149] and they were able to isolate the complexes $Mo_2(O_2CR)_4(py)_2$ (R = CH_3, C_6H_5) although it was several years before the first adduct was structurally characterised. An extensive study by Garner and Senior[163] led to the isolation of 1:1 adducts of the type $[Et_4N][Mo_2(O_2CCF_3)_4X]$ (X = Cl, Br, I, CF_3CO_2, $SnCl_3$) together with the 1:2 adducts $[EtN]_2[Mo_2(O_2CCF_3)_4X_2]$ (X = Br, I). Other adducts which have been prepared include $Mo_2(O_2CCHCl_2)_4(L)_2$ (L = C_5H_5N, $(CH_3)_2SO$[164]) $Mo_2(O_2CCF_3)_4(PR_3)_2$[163,165,166], $Mo_2(O_2CCF_3)_4(OPMe_3)_2$[165] and $Mo_2(O_2CCF_3)_4(CH_3OH)_2$[166].

Electrochemical studies[167] on the n-butyrate complex, $Mo_2(O_2C^nC_3H_7)_4$, in acetonitrile, dichloromethane and ethanol have revealed that the complex undergoes a quasi-reversible one electron oxidation (at $E_{\frac{1}{2}}$ values of +0.39, +0.45 and +0.30 V, respectively, versus a SCE) and $Mo_2(O_2CR)_4$ (R = C_2H_5, CMe_3, Ph) may also be oxidised chemically by iodine in dichloromethane to $[Mo_2(O_2CR)_4][I_3]$[162].

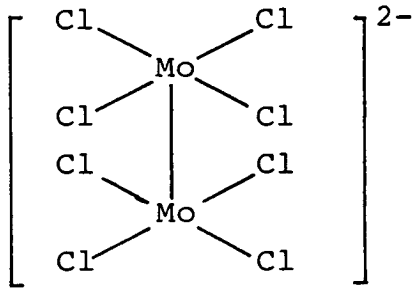
A large number of reactions have been reported in which some or all of the carboxylate groups are displaced. Examples of the former type include the synthesis of $[Ph_4As]_2[Mo_2(O_2CMe)_2Cl_4].2H_2O$[168,169] (42) from the

reaction of $Mo_2(O_2CMe)_4$ with $[Ph_4As]Cl$ in dilute hydrochloric acid, and the reaction with sodium acetylacetonate to give $Mo_2(O_2CMe)_2(acac)_2$[168]. The acetate groups are <u>trans</u> in the former and <u>cis</u> in the latter.



(42)

A wide range of complexes can be prepared by complete displacement of the carboxylate groups[146]. The most important of these are probably the octahalodimolybdate(II) anions. These are prepared by the reaction of $Mo_2(O_2CMe)_4$ at <u>ca</u>. 0°C with constant-boiling hydrohalic acid[170] and have been isolated as a variety of salts[171,172]. The anion $[Mo_2Cl_8]^{4-}$ (43) has been shown to be isostructural with $[Re_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$, in the salt $K_4[Mo_2Cl_8].2H_2O$[170].



(43)

A variety of other binuclear molybdenum halides are known (e.g. $[Mo_2Br_7]^{3-}$ [173], $[Mo_2X_6(H_2O)_2]^{2-}$ (X = Br, I) [174-176], $[Mo_2X_8H]^{3-}$ (X = Cl, Br, I) [177] etc.). Many of these can be directly prepared from $Mo_2(O_2CMe)_4$ or via the appropriate octahalomolybdate(II) anion.

The bridging acetate ligands of $Mo_2(O_2CMe)_4$ may also be displaced by other bidentate ligands. For example, the reaction of $Mo_2(O_2CMe)_4$ with methylsulphonic and trifluoromethylsulphonic acids produces the analogous ligand-bridged dimers $Mo_2(O_3SMe)_4$ [178] and $Mo_2(O_3SCF_3)_4$ [179]. Dimers containing bridging ligands with N,O, N,N and N,S donor sets have also been prepared by this route [146].

The final type of reaction is that in which the Mo-Mo quadruple bond is cleaved. Like many other low-oxidation state molybdenum compounds, dimers such as $Mo_2(O_2CMe)_4$ are easily oxidisable to oxomolybdenum species such as MoO_3 and MoO_4^{2-}. Although these oxidation reactions are not usually of any particular preparative significance, there are exceptions. For example, in hydrohalic acid, oxidation gives $[MoOX_4]^{2-}$ (X = Cl, Br, I) [180,181] and $[MoCl_5(H_2O)]^{2-}$ anions [182].

The ability of π-acceptor ligands to cleave the Mo-Mo quadruple bond is also well documented. Thus $Mo_2(O_2CMe)_4$ reacts with benzonitrile to yield $Mo(CNPh)_6$ [183] and with t-butyl isocyanide to give $Mo(CNCMe_3)_5(O_2CCH_3)_2$ [184]. Cleavage of the Mo-Mo bond also occurs with other π-acceptor

ligands such as CO and NO[146], possibly because axial coordination to produce L...M-M...L intermediates leads to a weakening of the π component of the M-M bond and subsequent reversion to monomers.

In contrast to the extensive chemistry associated with molybdenum(II) carboxylates, the analogous tungsten complexes $W_2(O_2CCF_3)_4$[185] and $W_2(O_2CC_6H_5)_4(THF)_2$[186] have only recently been prepared. Several earlier attempts to form these tungsten analogues by reaction of $W(CO)_6$ with carboxylic acids gave instead a series of unusual, trinuclear tungsten(IV) ions[187] of the type $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ or $[W_3O_2(O_2CR)_9]^-$. Metathetical reactions between quadruply bonded tungsten complexes and acetic acid (Equation [13]) were also unsuccessful. However, the reaction of $W_2(mhp)_4$[188] (mhp = 2-hydroxy-6-methyl-pyridine anion) with trifluoroacetic acid at low temperature gave the mixed ligand dimer $W_2(mhp)_2(O_2CCF_3)_2$[185]. This would not react any further with CF_3CO_2H, but would react with Na[mhp] to regenerate $W_2(mhp)_4$ (Equation [14]).

$$[Li(EtO)]_4[W_2(CH_3)_8] \text{ or } W_2Cl_4(PBu_3)_4 + HO_2CMe \longrightarrow W_2(O_2CMe)_4 \quad \ldots\ldots\ldots [13]$$

$$W_2(mhp)_4 \underset{\text{Namph}}{\overset{CF_3CO_2H}{\rightleftharpoons}} W_2(mhp)_2(O_2CCF_3)_2 \xrightarrow{CF_3CO_2} W_2(O_2CCF_3)_4 \quad \ldots\ldots\ldots [14]$$

The successful synthesis of the tungsten(II) tetracarboxylates has now been achieved[185,186] by employing strictly nonacidic conditions in order to prevent oxidative addition of acid, and concomitant bridge cleavage (see Equation [15] and [16]).

$$W_2Cl_6(THF)_4 \xrightarrow{2Na/Hg} [W_2Cl_4(THF)_4] \xrightarrow{4Na[O_2CCF_3]} W_2(O_2CCF_3)_4 \quad .....[15]$$

$$WCl_4 \xrightarrow[THF]{2Na/Hg} WCl_2 \xrightarrow[THF]{4Na[O_2CC_6H_5]} W_2(O_2CC_6H_5)_4(THF)_2 \quad .....[16]$$

The exclusion of acid is a necessary condition for these reactions to proceed as it has been previously found that the quadruple bonds in $W_2Cl_4(P^nBu_3)_4$ and W_2(2,4-dimethyl-6-oxypyrimidinate)$_4$ are destroyed by acid, leaving a single W-W bond in the former case and a double bond in the latter[189,190].

A preliminary investigation of the reactivity of the complex $W_2(O_2CCF_3)_4$ has shown that it will form the adduct $W_2(O_2CCF_3)_4(PPh_3)_2$ with triphenylphosphine, and that in concentrated aqueous hydrochloric acid the ions $[W_2Cl_9]^{3-}$ and $[W_2Cl_8H]^{3-}$ are generated[185].

Rhodium and Iridium

Rhodium(II) compounds are relatively rare (in comparison to those of Rh(I) and Rh(III)) and the tetracarboxylates consititute both the largest number and the most important examples. The dirhodium tetracarboxylates are isostructural with $Mo_2(O_2CR)_4$, although there are 14 valence electrons, rather than 8, to occupy the M-M molecular orbitals. Thus in terms of the simple picture, described earlier, after filling the σ, π and δ orbitals, there are still 6 electrons left to occupy the π^* and δ^* orbitals, giving a net Rh-Rh bond order of 1. Typically, the Rh-Rh bond lengths in such compounds are found in the range 2.35 - 2.45 Å which indicates they are rather strong single bonds.

Rhodium tetracarboxylates are usually obtained by reduction of rhodium(III) compounds, (in the presence of the carboxylate ligand); in alcoholic solution. Preparative methods involving both $M_3[RhCl_6]$[191,192] (M = K, Na etc.) and $Rh(OH)_3.H_2O$[193] have been used in the past while the most efficient general method now uses $RhCl_3.3H_2O$[194-196] (see Equation [17]).

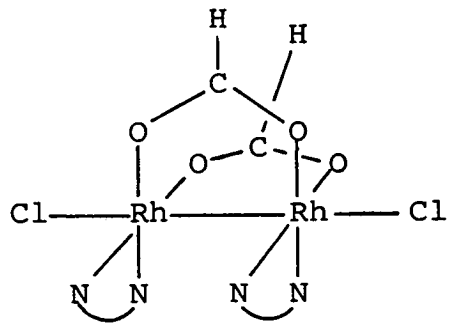
$$RhCl_3.3H_2O \xrightarrow[EtOH/\Delta]{RCO_2H + RCO_2Na} Rh_2(O_2CR)_4.x(EtOH) \quad \ldots.[17]$$

Recrystallisation of the green product from methanol gives $Rh_2(O_2CR)_4(MeOH)_2$ which on further heating gives $Rh_2(O_2CR)_4$. The acetate ligands in the latter

are then readily exchanged for other carboxylates by reaction with the desired acid[193,197,198]. The first structural determination of a $Rh_2(O_2CR)_4L_2$ compound was reported in 1970 for $Rh_2(O_2CMe)_4(H_2O)_2$[199] which together with many subsequent determinations[146] confirmed that these rhodium complexes are isostructural with their molybdenum analogues. A large variety of 1:2 adducts are now known, the largest group being those in which the axial ligands L are nitrogen donors, e.g. ammonia, pyridine, acetonitrile, nitric oxide and the $[NCX]^-$ (X = O, S, Se) ions etc.[146]. Dimethyl sulphoxide forms both 1:1[200] and 1:2[193,200] adducts, The $(CH_3)_2SO$ molecule is ambidentate in nature coordinating through sulphur with $Rh_2(O_2CR)_4$ (R= Me, Et) and through oxygen with $Rh_2(O_2CCF_3)_4$[201,202]. Axial ligands giving Rh-C bonds with $Rh_2(O_2CR)_4$ compounds are $[CN]^-$ [203], CO[204,205] and RNC[206]. As well as PPh_3 adducts[194,207], preparative and structural studies have also been reported for $Rh_2(O_2CMe)_4(PY_3)_2$ (Y = F[208], OPh[209], Ph, OMe[208]) and for $Rh_2(O_2CCF_3)_4(PY_3)_2$ (Y = Ph, OPh[210]).

These rhodium complexes also undergo reactions in which the carboxylate ligands are partially or totally displaced. For example the reaction of $Rh_2(O_2CMe)_4(H_2O)_2$ in methanol with dimethylglyoxime (Hdmg) gives $Rh_2(O_2CMe)_2(dmg)_2(H_2O)_2$. The water ligands are then readily displaced by PPh_3 and a crystal structure determination of this product shows that the acetate ligands have a cisoid arrangement[211].

Similarly the compound $Rh_2(O_2CH)_2(phen)_2Cl_2$ (44) has been shown to have cisoid formate ligands and axial chloride ligands[212].



(44)

(N⌒N = 1,10-phenanthroline)

Two examples of reactions in which all the carboxylate ligands are displaced but the Rh_2^{4+} unit preserved are: (a) the reaction of $Rh_2(O_2CMe)_4(MeOH)_2$ with Na[mhp] to give the complex $Rh_2(mhp)_4$[213], and (b) the reaction of $Rh_2(O_2CMe)_4$ with a concentrated aqueous solution of alkali metal carbonate to give $M_4[Rh_2(CO_3)_4]$ (M = Na, K, Cs)[214], in which the two metal atoms are bridged by four carbonato ligands.

The contrast between ease of formation of second versus third row transition metal carboxylates is even more marked here than it is for molybdenum and tungsten. There has only been one report of the preparation of an iridium tetracarboxylate complex[215], namely $Ir_2(O_2CMe)_4Cl_2$, by reaction of $H[IrCl_2(HCOO)_2]$, (prepared from $H_2[IrCl_6]$ and concentrated aqueous formic acid), with acetic acid. However, as there has been no subsequent verification or extension of this work, validity of the initial communication must be in considerable doubt.

Ruthenium and Osmium

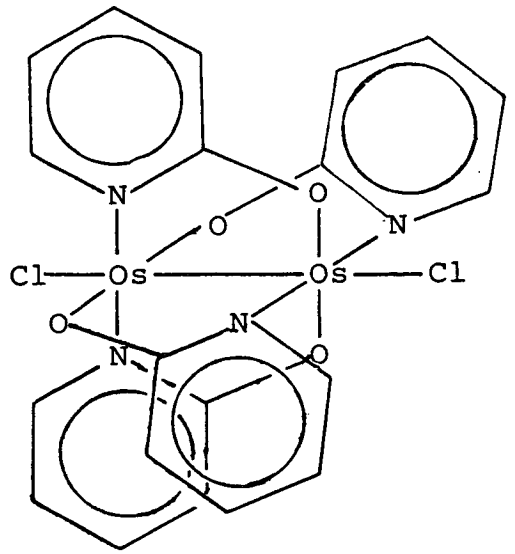
The unusual ruthenium tetracarboxylates $Ru_2(O_2CR)_4Cl$ (R = Me, Et, Pr^n) were first prepared by Stephenson and Wilkinson[216] by refluxing commercial "$RuCl_3xH_2O$" with carboxylic acid-anhydride mixtures. The preparation of the formate, $Ru_2(O_2CH)_4Cl$, was reported soon afterwards[217] and alternative syntheses for these complexes have now been published[218,219]. The first structural work dealt with the n-butyrate[220], $Ru_2(O_2CC_3H_7)_4Cl$. This was shown to consist of the familiar binuclear carboxylato-bridged units linked by single chloride ions into infinite zig-zag chains. The Ru-Cl distance (2.587(5) Å) is unusually long and is consistent with the fact that in solution the complex behaves as a 1:1 electrolyte[216]. A number of subsequent structure determinations on related compounds have confirmed the initial findings[221-223]. The compounds isolated by Stephenson and Wilkinson were reported to exhibit magnetic moments corresponding to three unpaired electrons[216] and more sophisticated measurements later confirmed this observation[224]. The ground state electronic configuration of the $[Ru_2(O_2CR)_4]^+$ cation is claimed to be $\sigma^2\pi^4\delta^2\pi^{*2}\delta^*$ [225,226], the $\pi^* < \delta^*$ order being the reverse of that normally encountered. Hence these complexes have a formal Ru-Ru bond order of 2.5.

As with the other carboxylate complexes described in this introduction, reactions involving substitution of both axial and/or equatorial ligands are known. Thus anion exchange reactions on $Ru_2(O_2CR)_4Cl$ (R = H, Me) have been used to exchange bromide, iodide, thiocyanate, nitrate and acetate for chloride[217], while carboxylate exchange reactions provide a route to the benzoate and monochloroacetate complexes[217]. The reactions of $Ru_2(O_2CMe)_4Cl$, with pyridine and PPh_3 have been claimed[216,219] to produce $Ru(O_2CMe)_2(py)_2$ and $Ru(O_2CMe)_2PPh_3$ respectively. The latter complex may be dimeric but in the absence of any crystallographic data the true identity of these materials remains unclear. In another example of facile Ru-Ru bond cleavage Wilkinson *et al* have reacted $Ru_2(O_2CMe)_4Cl$ with magnesium dialkyls (or diaryls) in the presence of trimethylphosphine and isolated the ruthenium(II) monomers *cis*-$Ru(CH_3)_2(PMe_3)_4$, $RuPh_2(PMe_3)_4$, $Ru[(CH_2)_2SiMe_2](PMe_3)_4$ and $Ru[(CH_2)_2CMe_2](PMe_3)_4$[227-229]. In addition the novel methylene-bridged diruthenium(III) compound, $Ru_2(CH_2)_3(PMe_3)_6$ has been isolated as a minor product from the reaction of $Ru_2(O_2CMe)_4Cl$ with dimethylmagnesium[230,231].

The displacement of the carboxylate ligands does not always lead to Ru-Ru bond cleavage. For example $Ru_2(O_2CMe)_4Cl$ reacts with LH_2 (the protonated form of dibenzotetraaza[14]annulene, $[C_{22}H_{22}N_4]^{2-}$) in ethanol to produce the dimer $[RuL]_2Cl$ as its ethanol solvate[232] in

which, despite the lack of any bridging ligands, the Ru-Ru bond has been retained.

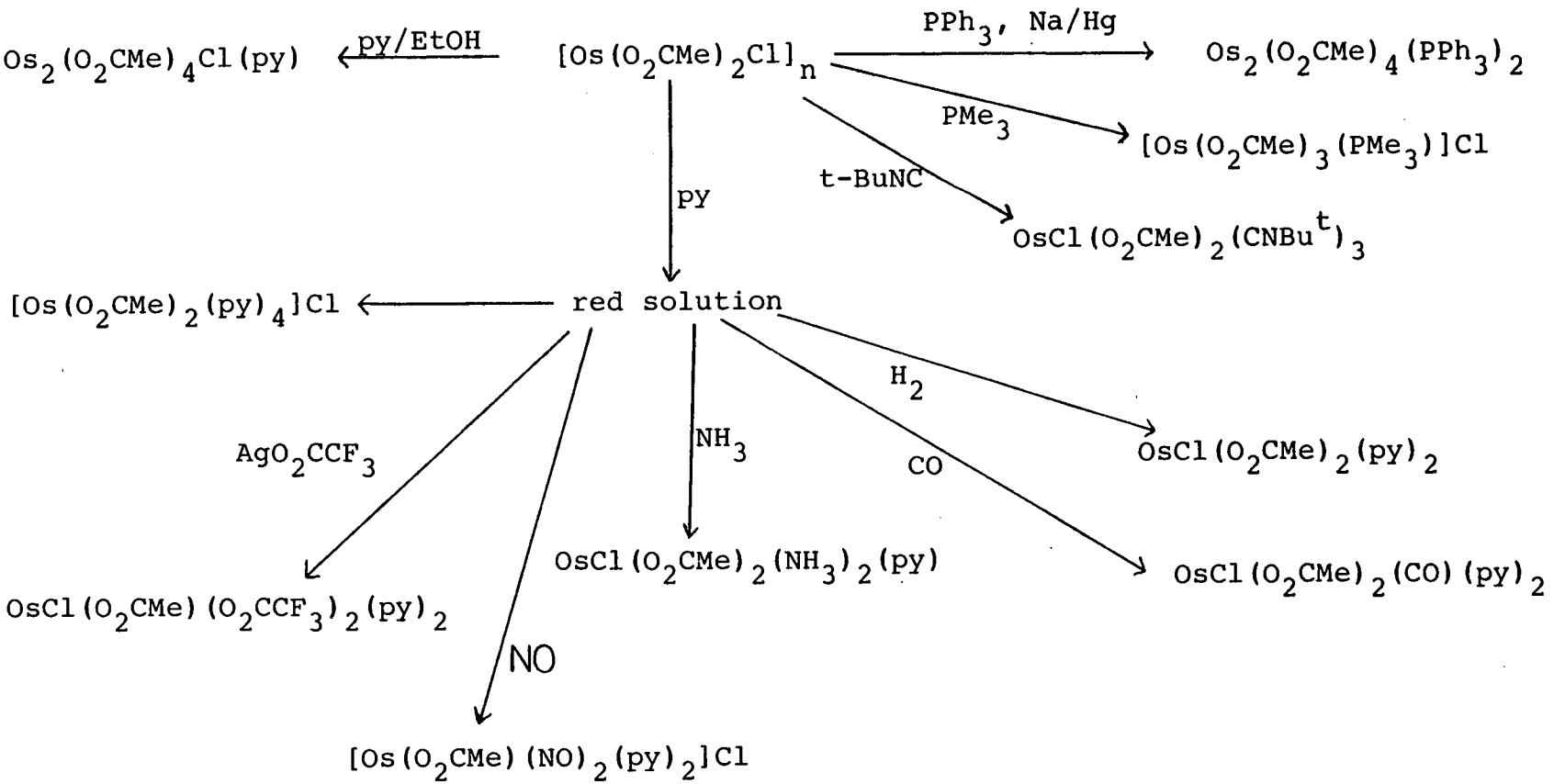
When the work to be described in this Chapter started there had been only one reported example of a binuclear osmium complex containing a multiple M-M bond. This was the complex $Os_2(hp)_4Cl_2$ (45) (hp = 2-hydroxypyridine anion), obtained by reaction of osmium(III)chloride with Hhp in refluxing ethanol[233]. Two crystal structure determinations (of the etherate and acetonitrile solvate) showed the complex had the expected geometry.



(45)

While this work was in progress, an independent report of the preparation of $[Os(O_2CMe)_2Cl]_n$ appeared in the literature[234]. Although the preparation described at that time is essentially identical to that reported in the next section, an alternative, more reliable, synthesis has been developed[235]. The initial communication also

Figure 4.4 Some reported reactions of $[Os(O_2CMe)_2Cl]_n$ (234)



reported that $[Os(O_2CMe)_2Cl]_n$ underwent a wide variety of reactions (see Figure 4.4). However it now appears that many of the compounds claimed to be formed are, upon closer examination, found to be mixtures[235].

4.2 The synthesis of osmium(III)chloro carboxylates, $Os_2(O_2CR)_4Cl_2$ (R = CH_3, C_2H_5, $^nC_3H_7$, CH_2Cl): X-ray structural analysis of $Os_2(O_2C^nC_3H_7)_4Cl_2$

As with the synthesis of many other dimeric transition metal carboxylates, the compound $Os_2(O_2CMe)_4Cl_2$ is prepared from a monomeric starting material[146]. Thus refluxing a solution of sodium hexachloroosmate(IV) in glacial acetic acid containing acetic anhydride and a small amount of concentrated hydrochloric acid for 6-8 hours produces a brown microcrystalline precipitate. The material is insoluble in all common organic solvents except pyridine with which it reacts, so that its molecular weight could not be determined in solution. However, it was sufficiently volatile for a weak parent ion peak to be observed (at m/e 687) in its mass spectrum. Fragmentation peaks due to successive loss of two chloride ions were also observed as was loss of a series of more complex organic fragments (see Section 4.4). The infrared mull spectrum shows strong bands at 1450 and 1380 cm^{-1}, indicating symmetrically coordinated acetate groups[93]. The spectrum also shows bands at 392 and 345 cm^{-1} probably attributable to ν(Os-O) and ν(Os-Cl) vibrational modes

respectively. Analytical data (see Table 4.1) fits for $Os_2(O_2CMe)_4Cl_2$ and the structure is presumably the usual tetraacetate bridged structure with terminal chlorine atoms, similar to that of $Re_2(O_2CMe)_4Cl_2$[236], and of the osmium butyrate discussed below. The composition of the residual reddish-brown solution produced in this reaction has not been ascertained. No precipitates were obtained upon addition of either large cations (Ph_4As^+, $Ph_3PhCH_2P^+$) or anions (BPh_4^-, PF_6^-), or upon slow evaporation of the solvent although species of the type $Os_3O(O_2CMe)_6(H_2O)_3$ might have been expected by analogy with the chemistry of ruthenium and molybdenum[146]. If the preparation is attempted using the lithium, ammonium or pottassium hexachloroosmates, or with a variety of salts of hexabromo-osmate(IV), then the reaction fails, probably because of the very low solubility of these salts. Similarly attempts to produce the bromo analogue, $Os_2(O_2CMe)_4Br_2$, by treatment of $Os_2(O_2CMe)_4Cl_2$ with LiBr were also unsuccessful.

Attempts to synthesise other osmium carboxylates $Os_2(O_2CR)_4Cl_2$ (R = C_2H_5, C_3H_7 <u>etc</u>) by direct reaction of $Na_2[OsCl_6]$ with the appropriate acid were less promising. For example, the reaction with propionic acid and its anhydride produced a small amount of a brown insoluble solid. The mass spectrum of this contained a parent ion peak, at m/e 705 corresponding to $[Os_2(O_2CC_2H_5)_3Cl_3]^+$ and elemental analysis supported this formulation. Unfortunately this preparation proved to be irreproducable. The reaction of $Na_2[OsCl_6]$ with n-butyric acid led only to extensive

decomposition. However, although it was not possible to synthesise other osmium carboxylates by direct reaction, certain of these can be obtained by exchange reactions with $Os_2(O_2CMe)_4Cl_2$ at elevated temperatures. Thus heating the acetate to 140-160°C in propionic or n-butyric acid gives dark green solutions which upon cooling yield the compounds $Os_2(O_2CR)_4Cl_2$ (R = C_2H_5, n-C_3H_7). Infrared spectra are similar to those of the acetate with peaks at 1478 and 1375 cm^{-1} (R = C_2H_5), 1471 and 1358 cm^{-1} (R = $^nC_3H_7$), indicative of symmetrically coordinated carboxylato groups[93]. Bands in the region 340-350 cm^{-1} and 390-400 cm^{-1} may be attributed to the Os-Cl and Os-O vibrations respectively. Analytical data (see Table 4.1) were consistent with the empirical formulae $[Os(O_2CR)_2Cl]_n$.

The binuclear nature of these species, which are more soluble than the acetate in organic solvents, has been confirmed by a variety of techniques. Thus, both compounds show mass spectral patterns containing strong parent ion peaks corresponding to the binuclear cations, $[Os_2(O_2CR)_4Cl_2]^+$. The loss of two successive chloride ions from these parents are observed, as is the loss of more complex organic fragments (see Section 4.4). The butyrate is sufficiently soluble in benzene for its molecular weight to be determined by osmometry. Values obtained at a variety of concentrations agree well with the proposed dimeric formulation. Unequivocal evidence

for the dimeric formulation is provided by the X-ray crystal structure determination of the butyrate, $Os_2(O_2C^nC_3H_7)_4Cl_2$, (see below).

The compound $Os_2(O_2CCH_2Cl)_4Cl_2$ is also obtained by reaction of $Os_2(O_2CMe)_4Cl_2$ with molten monochloroacetic acid. This complex is only slightly more soluble than the acetate and hence no solution data could be obtained. However, it does show the mass spectral pattern and infrared spectrum characteristic of the other osmium(III)carboxylates. Attempts to exchange $Os_2(O_2CMe)_4Cl_2$ with a variety of other acids (trifluoroacetic, monothioacetic, trichloroacetic, benzoic and oxalic acids) were unsuccessful, generally leading to the facile decomposition of any new, transient, osmium species formed.

X-ray Crystal structure of $Os_2(O_2C^nC_3H_7)_4Cl_2$

Details of the solution and refinement are given in the Experimental Section. Final atomic parameters are given in Table 4.2, selected bond lengths and angles in Table 4.3, an ORTEP diagram of the molecule in Figure 4.5, and a cell packing diagram in Figure 4.6.

The molecule is a dimer lying on a crystallographic inversion centre with each osmium ion exhibiting octahedral coordination. The Os-Os distance, 2.301(1) Å, is greater than that found in comparable diruthenium(II, III) compounds, (2.248 - 2.292 Å)[146] despite the greater

Figure 4.5 An ORTEP diagram of $Os_2(O_2CC_3H_7)_4Cl_2$

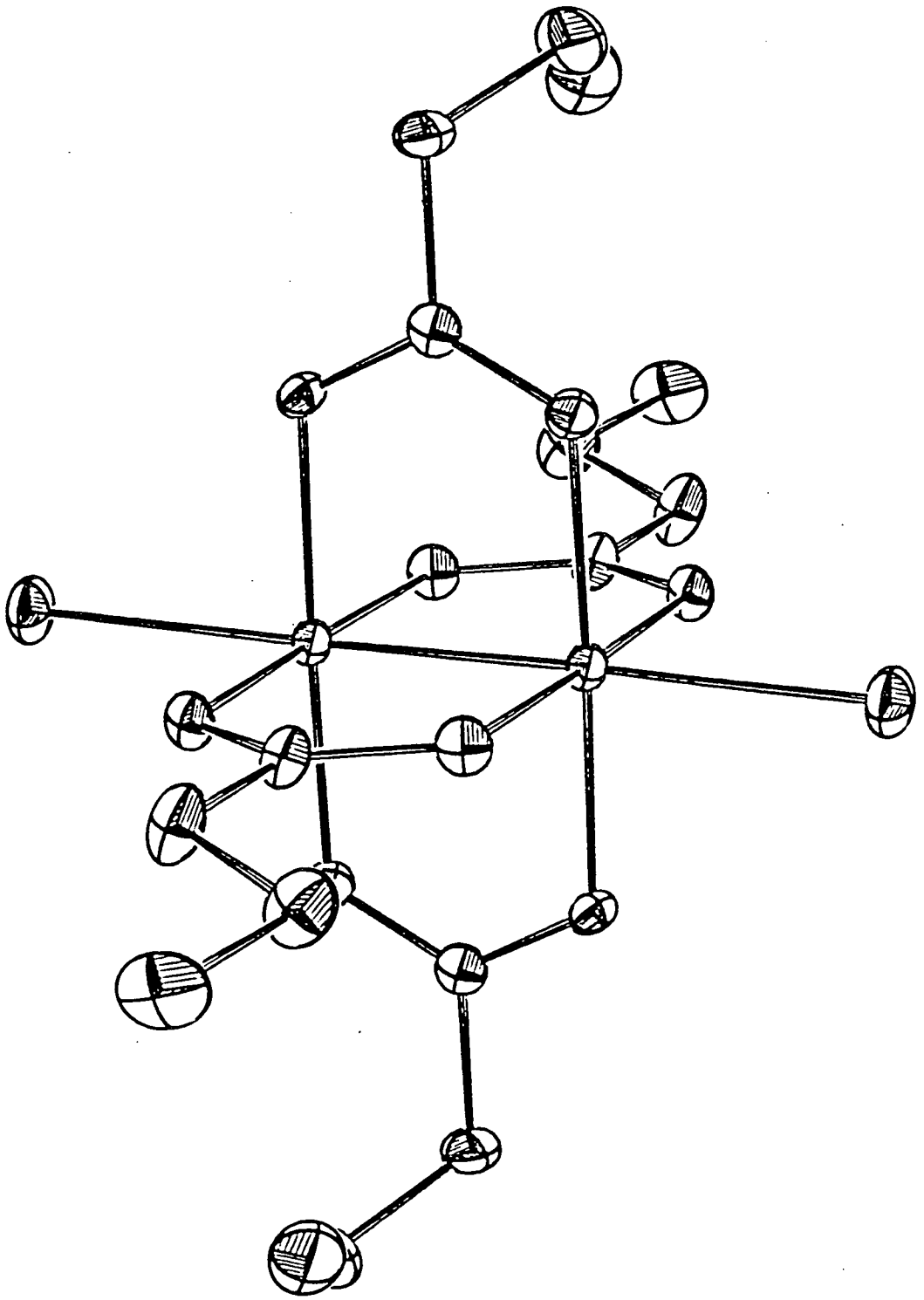
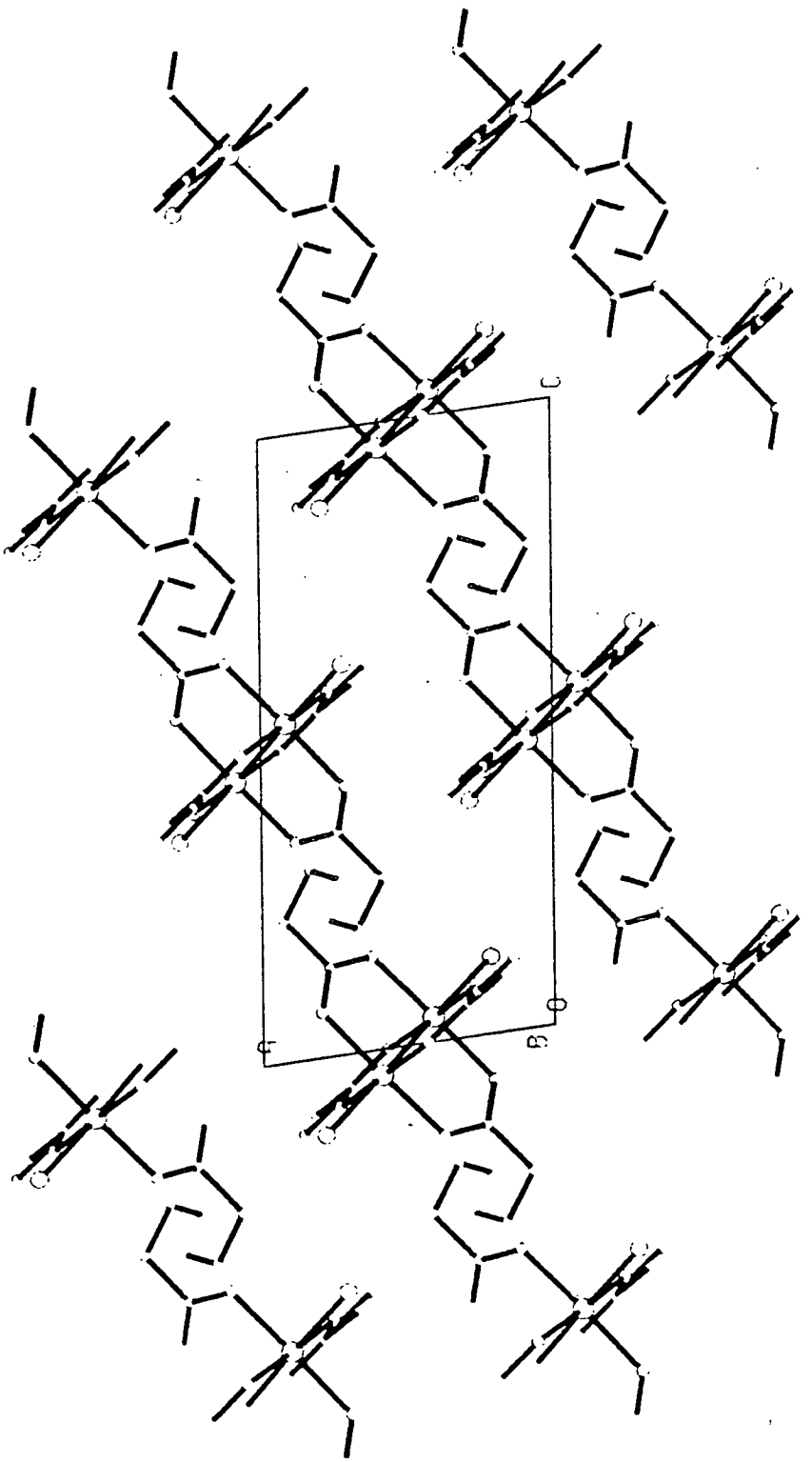


Figure 4.6 A cell packing diagram for $Os_2(O_2CC_3H_7)_4Cl_2$



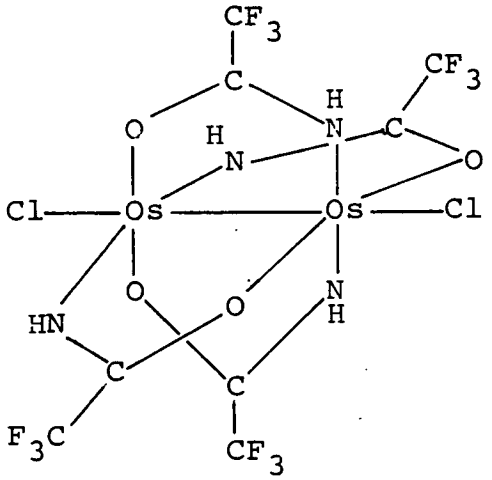
formal bond order (3.0 vs. 2.5). The Os-Cl distance, 2.417(3) Å is significantly less than those of related ruthenium complexes[146] which is in accord with the weak coordination of axial ligands in $Ru_2^{II,III}$ carboxylates. The observed Os-Os and Os-Cl distances are significantly less than those of the closely related $[Os_2(hp)_4Cl_2].2MeCN$ (hp = 2-hydroxypyridine anion), namely 2.357(1) and 2.505(5) Å respectively[233]. The twist angles O(1)-Os-Os*-O(2) and O(3)-Os-Os*-O(4) of 0.3° and 0.6°, respectively, are less than the average of 5.5° reported for the 2-hydroxypyridinato complex. The reason for this is probably that in the carboxylato complexes there is little or no repulsive interaction between bridging and terminal ligands. The twisting reported in the 2-hydroxopyridinato compound arose from the interaction between the hydrogen in the 6-position on the pyridine rings and the terminal chloride ions. This twisting may give rise to less orbital overlap and hence a slight increase in the Os≡Os distance compared to that reported here; that is, the less distorted ligands allow the metal atoms to lie closer together. Finally, the n-butyrate groups exhibit both gauche [C(4)-C(3)-C(2)-C(1) = 54°] and trans [C(8)-C(7)-C(6)-C(5) = 176°] conformations.

4.3 Some reactions of $Os_2(O_2CR)_4Cl_2$ compounds

The three types of reactions common to binuclear tetra-μ-carboxylato transition metal complexes (see Section 4.1) have already been described. As an example of the first category, namely (a) reactions in which the terminal ligands are displaced but the $M_2(O_2CR)_4$ unit remains intact, Wilkinson et al[234] have reported that the reaction of $Os_2(O_2CMe)_4Cl_2$ with PPh_3 gives $Os_2(O_2CMe)_4(PPh_3)_2$. The majority of the reactions found here however fall into the latter two groups, i.e. (b) reactions in which one set of bridging ligands are displaced by a second set, or (c) reactions leading to complete disruption of the dimer structure. Moreover, it appears that the diosmium compounds are very reactive and most reagents totally disrupt the structure. Only two examples of reactions in which bridge exchange, (other than with other carboxylates), has occurred have so far been discovered.

The acetate reacts with 2-hydroxypyridine in methanol to yield a dark red-purple solid. Analytical and mass spectral data (see Experimental Section) indicate that the compound is the known $Os_2(hp)_4Cl_2$, previously prepared by reaction of $OsCl_3$ with 2-hydroxypyridine in ethanol[233]. Like the carboxylates (see Section 4.7) this compound is also paramagnetic with values of μ_{eff} in CH_2Cl_2 (1.44 BM/Os at 295 K) consistent with considerable antiferromagnetic interaction between osmium(III) centres (see Section 4.7).

The other example of bridge exchange is the reaction of $Os_2(O_2C^nC_3H_7)_4Cl_2$ with molten 2,2,2-trifluoroacetamide. It is necessary to use the n-butyrate rather than the acetate because the product formed $[Os(ONHCCF_3)_2Cl]_n$ (46) is so insoluble that it cannot be separated from unreacted, equally insoluble osmium acetate. In fact, the low solubility and lack of volatility makes it impossible to determine unequivocally the structure of this complex although by analogy with studies on $Rh_2(ONHCCF_3)_4$ [237] it is likely that it is a binuclear one of the type shown below.



(46)

In all the other reactions that have been studied to date cleavage of the Os-Os triple bond occurs. The reaction of transition metal carboxylates with hydrogen halides has been shown, in many cases, to give complexes in which the M-M bond has been retained. For example, the anions $[Re_2X_8]^{2-}$ (X = Cl, Br, I) were obtained when

$Re_2(O_2CC_6H_5)_4Cl_2$ is treated with gaseous HX in methanol[238] and $[Mo_2Cl_8]^{4-}$ is formed from $Mo_2(O_2CMe)_4$ and concentrated hydrochloric acid[170]. However addition of $[Ph_3(PhCH_2)P]Cl$ to the yellow solution obtained upon dissolving $Os_2(O_2CMe)_4Cl_2$ in concentrated hydrochloric acid gave a lemon yellow precipitate, identical in its infrared spectrum and electrochemical behaviour to $[Ph_3(PhCH_2)P]_2[OsCl_6]$ which is readily prepared by direct reaction of $[Ph_3(PhCH_2)P]Cl$ with $Na_2[OsCl_6]$[239] (see Experimental Section). Similarly, treatment of the acetate with aqueous HBr containing KBr, followed by addition of $[Ph_3(PhCH_2)P]Cl$ gives $[Ph_3(PhCH_2)P]_2[OsBr_6]$, as demonstrated by comparison with a genuine sample of this compound.

The reaction of $Mo_2(O_2CMe)_4$ with sodium acetylacetonate (Na[acac]) leads to the displacement of only two of the acetate ligands and the formation of $Mo_2(O_2CMe)_2(acac)_2$ in which the two bridging acetates are cis and the acetylacetonate ligands are chelating[240]. In contrast, the reaction of $Os_2(O_2CMe)_4Cl_2$ with Na[acac] leads to extensive decomposition. However, reaction of the acetate with neat acetylacetone under reflux conditions gives a deep red solution from which, on cooling, a small amount of a rather insoluble microcrystalline red solid could be isolated. Analytical data and its infrared spectrum were consistent with the formulation t-$Os^{IV}(acac)_2Cl_2$. Although the complex is too insoluble for its molecular weight to be determined in solution, it was sufficiently volatile for a parent ion peak (at m/e 459) to be observed

in its mass spectrum. A fragmentation peak due to loss of chloride ion was also clearly observed. Furthermore the magnetic moment of 1.29 BM at 288 K is typical of an osmium(IV) complex as is its electrochemical behaviour (see Section 4.5).

The reaction of an aqueous suspension of the acetate with an excess of $Na[S_2CNMe_2].3H_2O$ gives a small amount of a dark red powder. The compound is both involatile and rather insoluble. The infrared spectrum contains only bands due to bound $[S_2CNMe_2]^-$ and a ν(Os-Cl) at 335 cm^{-1}. Electrochemical measurements strongly indicate the osmium ion is in oxidation state IV. On the basis of this evidence and the analytical data (see Table 4.1), the compound is best formulated as $Os^{IV}(S_2CNMe_2)_2Cl_2$.

Thus, it would appear that reaction of osmium(III) carboxylates with HX and acacH leads to oxidation of the osmium(III) centres and concomitant bridge cleavage. The tendancy for the quadruple bonds in a variety of ditungsten complexes to undergo oxidative addition reactions, and partial bridge cleavage, on treatment with acids has already been noted[241].

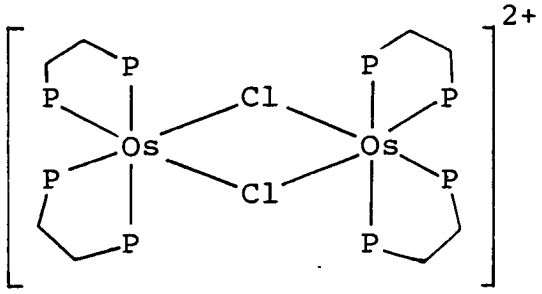
In contrast to the reactions described above, where oxidation of the metal was a common feature, interaction of the acetate with the donor ligands 2,2'-bipyridyl, 1,10-phenanthroline and $Ph_2P(CH_2)_2PPh_2$ leads to reduction of the metal and the isolation of a series of osmium(II) complexes.

Thus, if the acetate is refluxed with an excess of 2,2'-bipyridyl in methanol and the resulting green solution treated with $Na[BPh_4]$, the well-known green $[Os(bipy)_3][BPh_4]_2$ is precipitated. Likewise, treatment with 1,10-phenanthroline gives the equally well-known $[Os(phen)_3][BPh_4]_2$. These formulations are based on analytical data and comparison of their electrochemical behaviour and electronic spectra with those previously reported[242,243].

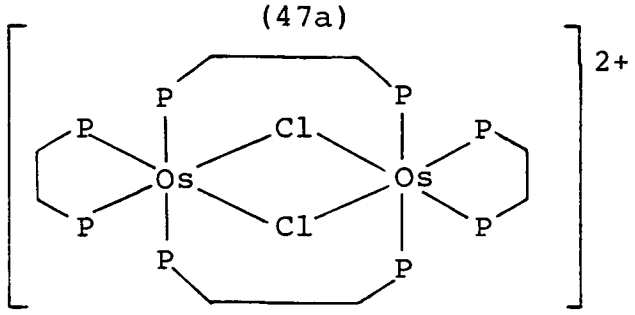
Although the acetate reacts with pyridine and teriary phosphines it proved impossible to isolate any pure species.

However, the acetate reacts with the diphosphine, $PPh_2(CH_2)_2PPh_2$, in methanol to give a low yield of a non-conducting pale yellow solid. The infrared spectrum of this product contained no bands assignable to acetate ligands although it did contain bands typical of the phosphine. In addition a single ν(Os-Cl) band, at 343 cm^{-1}, was observed. The compound was sufficiently volatile for its mass spectrum to be recorded. A parent ion peak, at m/e 1057, arising from $[Os(diphos)_2Cl_2]^+$ is observed, as are fragmentation patterns due to successive loss of two chloride ions. The $^{31}P-\{^1H\}$ n.m.r. spectrum in CD_2Cl_2 at 301 K contained only a singlet, at δ7.30 ppm, indicating a <u>trans</u> configuration for the diphosphines. The compound is thus best formulated as <u>trans</u>-$[OsCl_2(diphos)_2]$[244].

Treatment of the dark-grey filtrate, obtained in the reaction described above, with $Na[BPh_4]$ gives a higher yield of a blue-grey precipitate. The $^{31}P-\{^1H\}$ n.m.r. in CD_2Cl_2 at 301 K contains two triplets, at δ36.5 and 5.5 ppm ($^2J_{P-P}$ = 4.4 Hz). The infrared spectrum does not contain any bands assignable to acetate groups although bands due to $PPh_2(CH_2)_2PPh_2$ and $[BPh_4]^-$ are present as is a band at 285 cm^{-1} assigned to ν(Os-Cl) bridging modes. Analytical data fit for the empirical formulation $[Os(diphos)_2Cl][BPh_4]$ but conductivity measurements in CH_3NO_2 indicate that the complex is a 2:1 electrolyte (see Experimental Section). The complex is thus best formulated as $[Os_2(diphos)_4Cl_2][BPh_4]_2$ (47). On present evidence it is impossible to distinguish between the two structures postulated for the dication. Furthermore, the mechanism by which many of the complexes described above are formed is far from clear. In particular the mechanism for chloride transfer, which is a feature of many of the reactions, is still obscure.



(47a)



(47b)

Finally, although $Os_2(O_2CMe)_4Cl_2$ reacts with a far wider range of ligands than described here, in general these reactions lead either to extensive decomposition or an inseparable mixture of products. Therefore only those reactions in which the nature of the products is clear have been described, although in some cases further studies are required to clarify the nature of these reaction products.

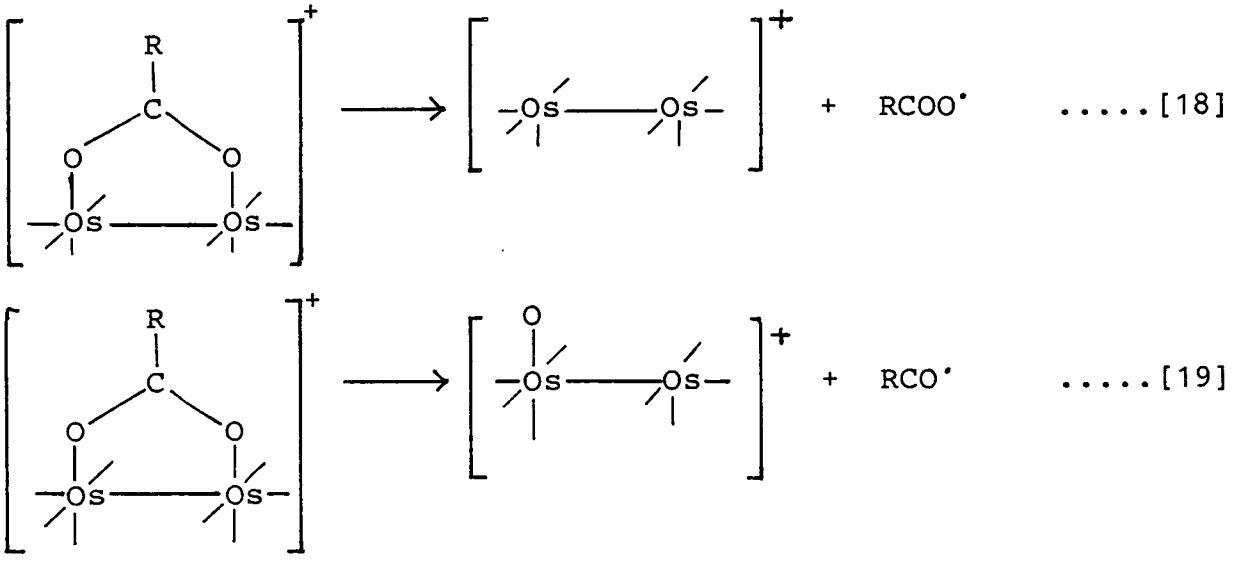
4.4 An interpretation of the mass spectral fragmentation patterns for the osmium carboxylates, $Os_2(O_2CR)_4Cl_2$ (R = Me, C_2H_5, $^nC_3H_7$, CH_2Cl)

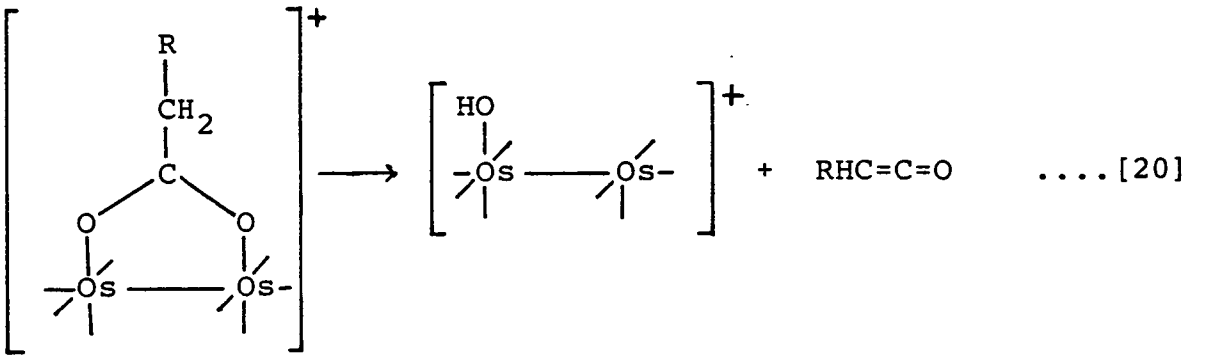
A number of mass spectral studies have been carried out on the closely related dimolybdenum(II) carboxylates[154,155,245]. The results of these studies in many ways parallel the work on diosmium(III)carboxylates reported here. The diosmium(III) carboxylates give mass spectra in which the molecular ion peak, although not dominant, is clearly observed. The large number of isotopes for osmium and the presence of two osmium atoms in the molecule leads to a molecular ion which gives nine different peaks with distinctive ratios. This pattern is a convenient fingerprint for any compound with the Os_2^{6+} unit. The mass spectra of the tetra-μ-carboxylatodichlorodiosmium(III) complexes appear in Figures 4.7-4.10. Masses of ions refer to the ion in which the total osmium mass is 380 amu.

For coordination compounds it has been demonstrated that prominent ions in their mass spectra are frequently associated with species having the metal ion in its most

common oxidation state[246-252]. The data in Figures 4.6 - 4.9 show that oxidation states for the osmium ions of +2 to +4 are encountered.

In addition to fragmentation patterns due to loss of chloride ions, more complex fragmentation patterns due to loss of a variety of organic moieties, are observed. Three major pathways (see Equations [18], [19] and [20]) for fragmentation are evident. The loss of both chloride ions is not necessarily a precursor to loss of organic fragments. Indeed there is evidence that one of the more favourable pathways is the loss of one chloride ion followed by subsequent loss of a RCO· radical or RCH=C=O fragment. Indeed, the fragmentation pattern corresponding to loss of two chloride ions from $[Os_2(O_2CR)_4Cl_2]^+$ is weak in all the spectra. Furthermore, in none of the spectra examined was it possible to distinguish any mononuclear osmium fragments.



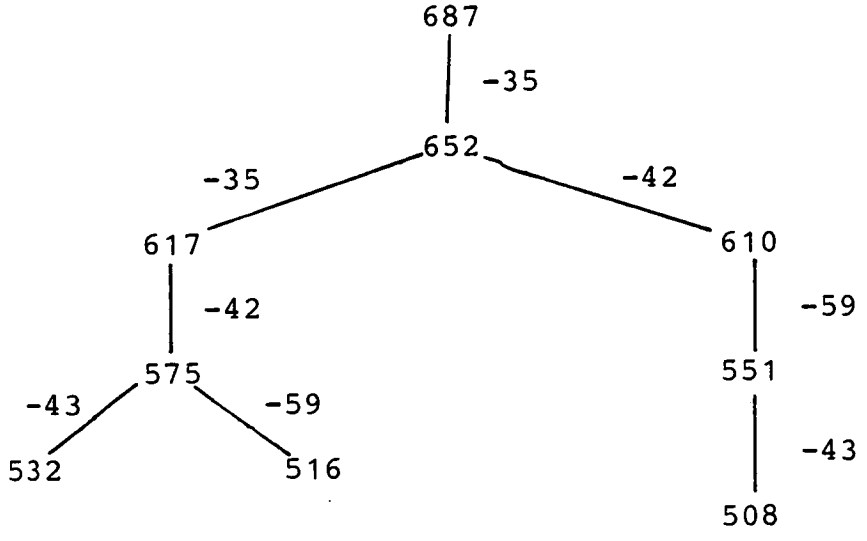


....[20]

The various fragmentation pathways are not independent of one another and the data indicate that none may succeed by itself. For example, in the case of the acetate complex (see Figure 4.7) two successive or simultaneous losses of $MeCOO^{\bullet}$, $MeCO^{\bullet}$ or $CH_2=C=O$ are not observed.

To an extent the failure of any one fragmentation to succeed itself may be viewed as a reflection of the narrow range of oxidation states available to the metal. The reactions shown in Equations [18] and [19] result, respectively, in a reduction and oxidation of the binuclear unit. These may not succeed themselves because it would lead to an unfavourable oxidation state, i.e. one outside the range +2 to +4. The reaction shown in Equation [20] leaves the binuclear unit in the same oxidation state. Figures 4.8 and 4.9 contain the mass spectral analysis for the proprionate and n-butyrate which are quite analogous to the acetate in the types of fragments lost although the details of the analysis differ. In the case of the monochloro-acetate, the fragmentation pattern is complicated by the fact that chloride ion may be lost from either of two sites (see Figure 4.10). It would be convenient to

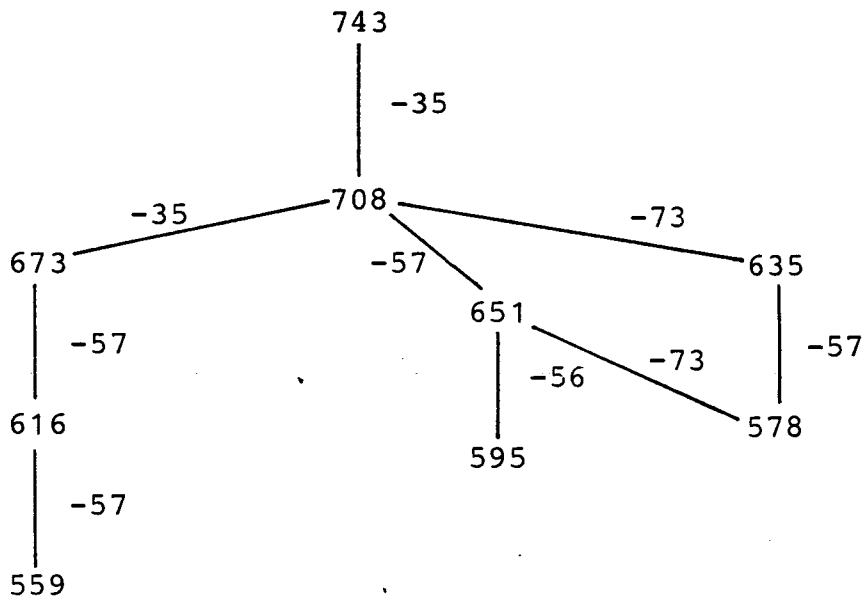
Figure 4.7 The mass spectral fragmentation pattern of $Os_2(O_2CMe)_4Cl_2$



m/e	Species	Ox. St. per Os
687	$Os_2Ac_4Cl_2^+$	3.5
652	$Os_2Ac_4Cl^+$	3.0
617	$Os_2Ac_4^+$	2.5
575	$Os_2Ac_3OH^+$	2.5
551	$Os_2Ac_2ClOH^+$	2.5
532	$Os_2Ac_2OOH^+$	3.0
516	$Os_2Ac_2OH^+$	2.0
508	$Os_2AcClOOH^+$	3.0
610	$Os_2Ac_3ClOH^+$	3.0

Ac = O_2CMe

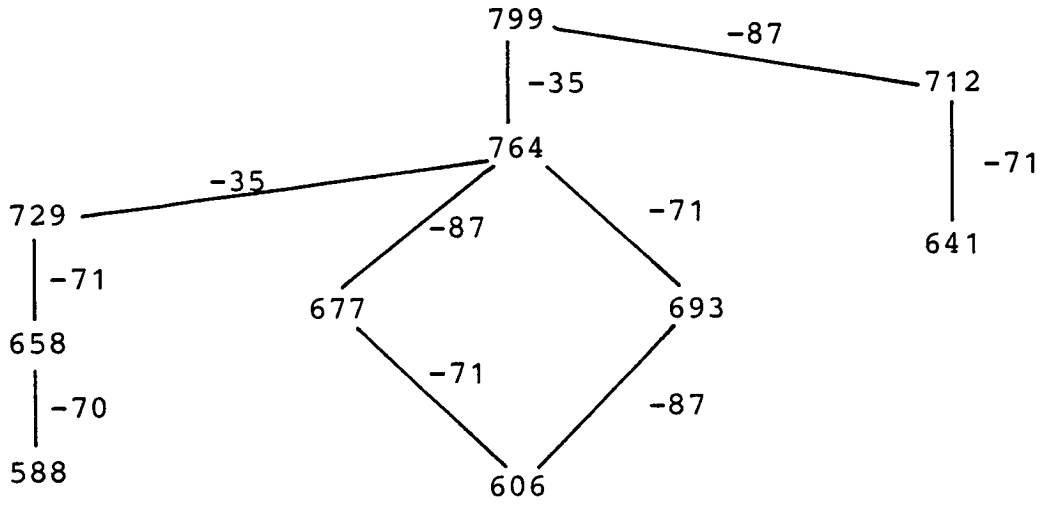
Figure 4.8 The mass spectral fragmentation pattern for $Os_2(O_2CC_2H_5)_4Cl_2$



m/e	Species	Ox.St. per Os
743	$Os_2Pr_4Cl_2^+$	3.5
708	$Os_2Pr_4Cl^+$	3.0
673	$Os_2Pr_4^+$	2.5
651	$Os_2Pr_3ClO^+$	3.5
635	$Os_2Pr_3Cl^+$	2.5
616	$Os_2Pr_3O^+$	3.0
595	$Os_2Pr_2ClOH^+$	2.5
578	$Os_2Pr_2ClO^+$	3.0
559	$Os_2Pr_2OO^+$	3.5

Pr = $O_2CC_2H_5$

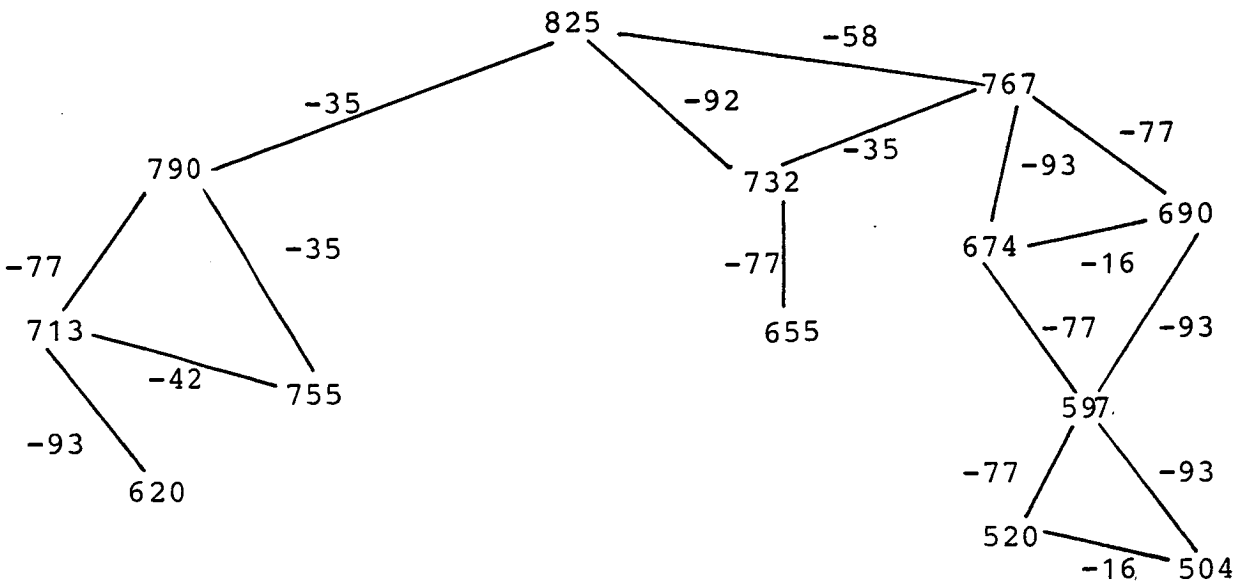
Figure 4.9 The mass spectral fragmentation pattern of $Os_2(O_2C^nC_3H_7)_4Cl_2$



m/e	Species	Os. St. per Os
799	$Os_2Bu_4Cl_2^+$	3.5
764	$Os_2Bu_4Cl^+$	3.0
729	$Os_2Bu_4^+$	2.5
712	$Os_2Bu_3Cl_2^+$	3.0
693	$Os_2Bu_3ClO^+$	3.5
677	$Os_2Bu_3Cl^+$	2.5
658	$Os_2Bu_3O^+$	3.0
641	$Os_2Bu_2Cl_2O^+$	3.5
606	$Os_2Bu_2ClO^+$	3.0
588	$Os_2Bu_2OOH^+$	3.0

Bu = $O_2CC_3H_7$

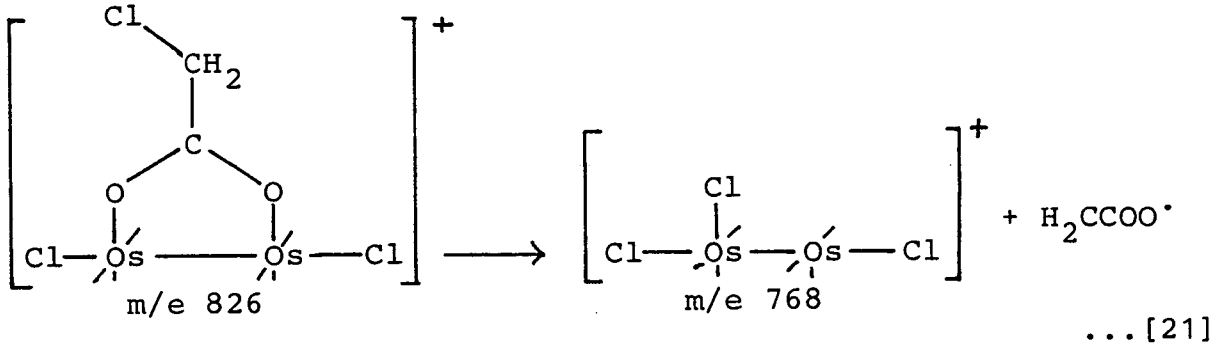
Figure 4.10 The mass spectral fragmentation pattern of $Os_2(O_2CCH_2Cl)_4Cl_2$



m/e	Species	Ox. St. per Os
825	$Os_2Ac_4Cl_2^+$	3.5
790	$Os_2Ac_4Cl^+$	3.0
767	$Os_2Ac_3Cl_3^+$	3.5
755	$Os_2Ac_4^+$	2.5
732	$Os_2Ac_3Cl_2^+$	3.0
713	$Os_2Ac_3ClO^+$	3.5
690	$Os_2Ac_2Cl_3O^+$	4.0
674	$Os_2Ac_2Cl_3^+$	3.0
655	$Os_2Ac_2Cl_2O^+$	3.5
620	$Os_2Ac_2ClO^+$	3.0
597	$Os_2AcCl_3O^+$	3.5
520	$Os_2Cl_3OO^+$	4.0
504	$Os_2Cl_3O^+$	3.0

Ac = O_2CCH_2Cl

assume that chloride ion was preferentially lost from the metal site. However, upon examining the spectra it is obvious that this need not be the case. In particular the peak at m/e 768 can only arise from loss of 58 amu from the parent ion $[Os_2(O_2CCH_2Cl)_4Cl_2]^+$ in the process shown below, (see Equation [21]), in which chloride transfer from the organic ligand to metal takes places.



...[21]

Additionally loss of an oxygen radical (O•) may be possible for the monochloroacetato complexes (e.g. m/e 697→ 675, m/e 521 → 505). Interestingly there is no evidence for the loss of either carbon monoxide or carbon dioxide from any of these compounds although loss of the latter is the major fragmentation pathway for $Mo_2(O_2CH)_4$ (245).

4.5 The electrochemical behaviour of some osmium complexes

The possibility of discrete redox changes in metal-metal bonded binuclear complexes is of interest for a number of reasons. For example, one-electron transfer steps should generate mixed valence compounds and if the redox active orbital is intimately involved in metal-metal bonding then structural changes should accompany electron transfer (e.g. ν(M-M)). Little work has been reported on complexes of the type $M_2(O_2CR)_4$ or $M_2(O_2CR)_4L_2$ although more extensive studies have been carried out on a variety of $[M_2X_8]^{n-}$ complexes. The two studies of particular relevance to this discussion are the earlier reports of the electrochemical behaviour of $Mo_2(O_2CC_3H_7)_4$[167] and $Ru_2(O_2CC_3H_7)_4Cl$[224].

Cotton and Pederson[167] studied the electrochemical behaviour of $Mo_2(O_2C^nC_3H_7)_4$ with the view that the n-butyrate complex was representative of the tetracarboxylato-dimolybdenum complexes. The electrochemical behaviour of the complex was examined in a variety of solvents (acetonitrile, dichloromethane and ethanol) and it was found to undergo an oxidation reaction, to form the cation $[Mo_2(O_2CC_3H_7)_4]^+$, at c.a. +0.4 V vs sce in all the solvents. However, the observation of a large separation between cathodic and anodic peaks (290 - 380 mV at V = 100 mVs^{-1}), the characteristic variation in ΔE_p with scan rate (ν), and that for ν = 5 mVs^{-1}, i_p^c/i_p^a = 0, in ethanol, were interpreted as being characteristic of an

almost irreversible charge-transfer mechanism (see Equation [22]).

$$[Mo_2(O_2CC_3H_7)_4]^+ + e \overset{E_{\frac{1}{2}}}{\rightleftharpoons} Mo_2(O_2CC_3H_7)_4$$

$$\Big\downarrow k$$

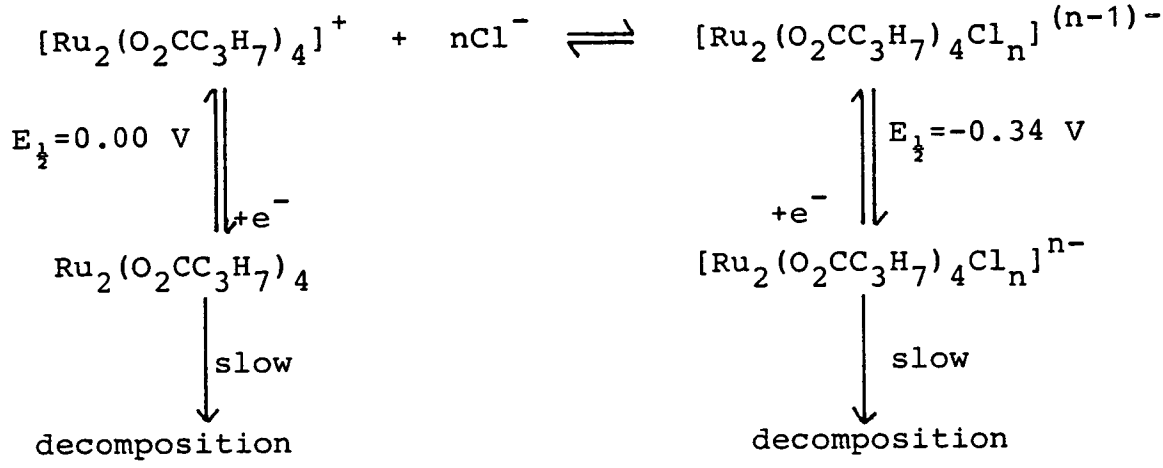
decomposition ....[22]

A subsequent study[253] on $Mo_2(O_2CMe)_4$ in acetone showed that this exhibited a quasi-reversible oxidation at +0.51 V vs Ag/AgCl and a much closer approach to fully reversible charge transfer behaviour. Interestingly, an analogous study on $Mo_2(O_2CCF_3)_4$ showed no oxidations or reductions in the available range, i.e. -1.8 V to +1.5 V[253].

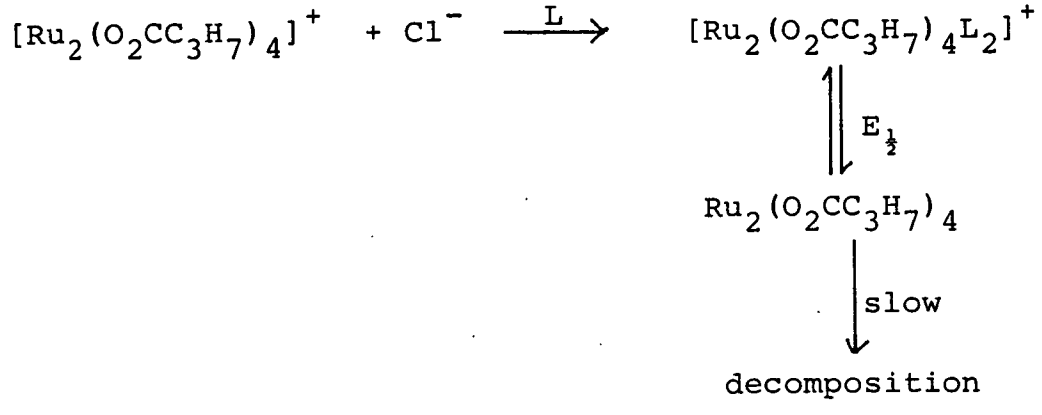
In contrast, the electrochemical behaviour of $Ru_2(O_2CC_3H_7)_4Cl$ is complex, and highly dependant on the solvent used[224]. Complicated and completely irreversible processes were observed below -1.1 V and above +1.6 V vs SCE. The only reversible reaction observed was a reduction in the potential range 0 to -0.4 V, with the exact voltage being dependent on the medium. In a dichloromethane solution a two step reduction was observed ($E_{\frac{1}{2}}$ = 0.00 and -0.34 V vs sce), the ratio of one peak current to another being dependent on the concentration of chloride ions present. Investigations carried out in CH_3CN and ethanol only showed a one-electron quasi-reversible reduction at a variety of scan rates and chloride concentrations. These results were interpreted as shown in Scheme 4.1.

Scheme 4.1 The electrochemical behaviour of $Ru_2(O_2CC_3H_7)_4Cl$

(a) Solvent = CH_2Cl_2



(b) Solvent = donor ligand

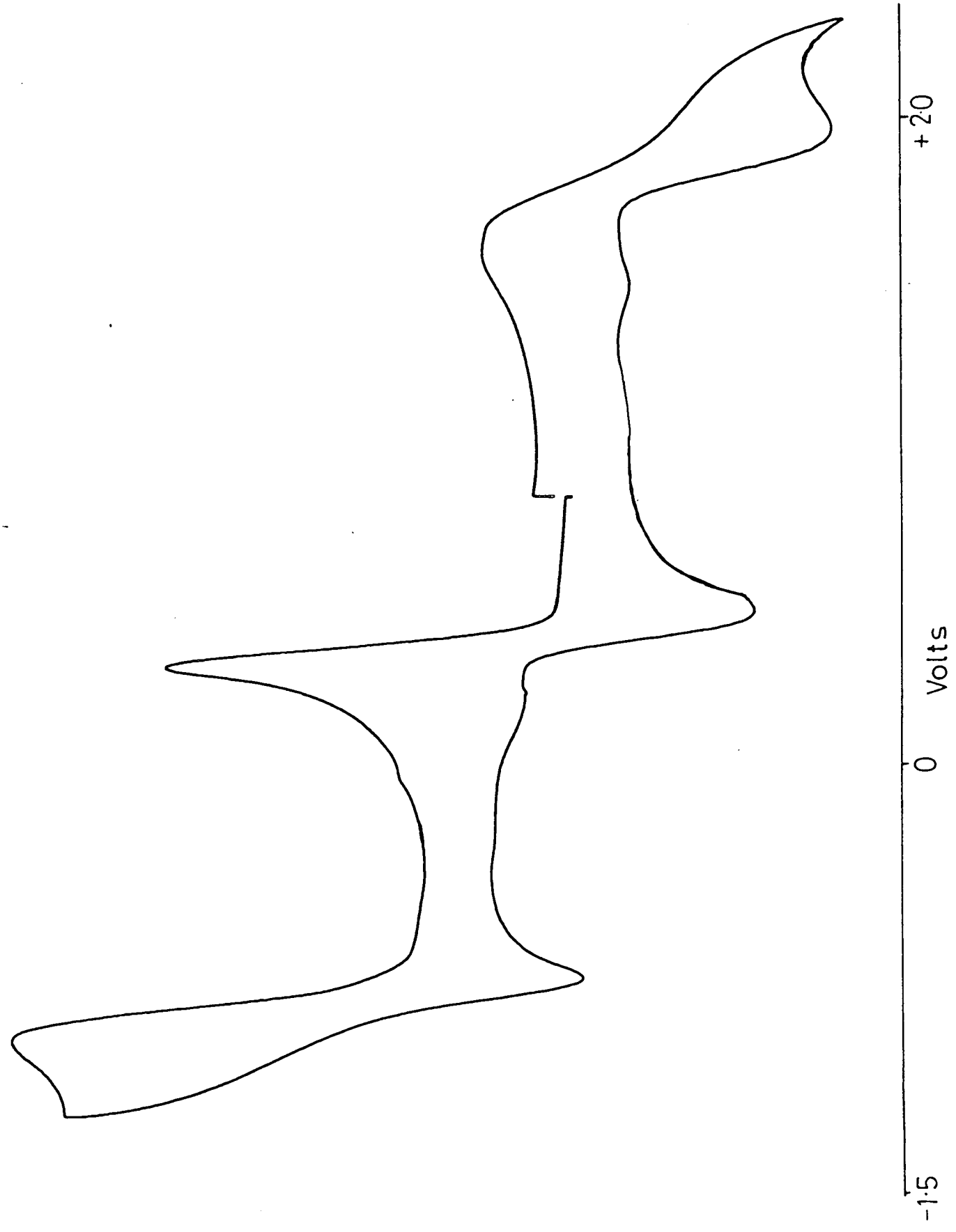


In the case of the osmium complexes, $Os_2(O_2CR)_4Cl_2$, both the propionate and n-butyrate are sufficiently soluble for their electrochemical behaviour to be studied in some detail. Cyclic (CV) and alternating current (acV) voltammetric measurements in CH_2Cl_2/0.25 M Bu_4NBF_4 at 293 K show that both compounds undergo a facile one-electron, reversible, oxidation at +0.57 and +0.53 V vs Ag/AgI, respectively. For the n-butyrate the reversible nature of the electron transfer is characterised, at 293 K, by a ratio i_p(anodic)/i_p(cathodic) = 1, at all scan rates (ν)

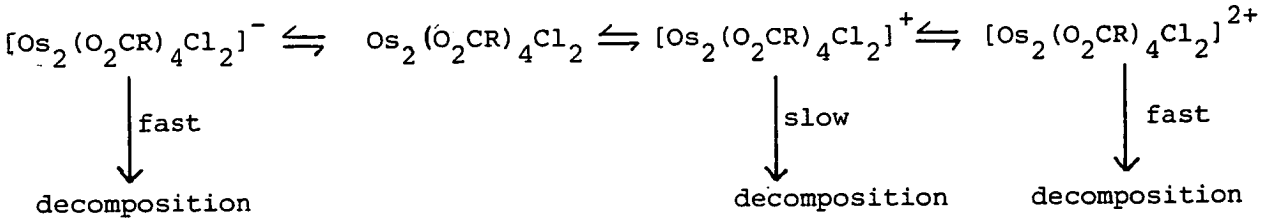
from 50-500 mVs^{-1} and a peak to peak separation, ΔE_p, of 60 ± 5 mV. The one-electron nature of the process is confirmed by the acV peak width at half height (90 mV independent of frequence (ω), in the range 100-500 Hz) and by the characteristic diffusion coefficient D = 1.12 x 10^{-5} cm^2s^{-1}. In addition the propionate exhibits irreversible oxidation (+1.89 V) and reduction (-1.31 V) waves and the butyrate shows similar peaks at +1.84 and -1.00 V. On cooling some return wave characteristics develop but even at 213 K these processes never attain full reversibility (see Figure 4.11). Hence this electrochemical evidence suggests that the formally mixed valence $[Os_2^{II,III}(O_2CR)_4Cl_2]^-$ anions are unstable in contrast to the corresponding ruthenium complex, $Cs[Ru_2(O_2CMe)_4Cl_2]$, whose X-ray structure has been reported[221].

It was hoped that controlled potential electrogeneration of the $Os_2^{III,IV}$ cations, $[Os_2(O_2CR)_4Cl_2]^+$, would enable their magnetic and spectroscopic properties to be determined. However, preliminary studies, using the OTTLE technique, indicate that on bulk electrogeneration these cations are too unstable at 228 K for even <u>in situ</u> measurements of their properties to be obtained. This result is both disappointing and surprising as the removal of an antibonding electron (from the δ^* orbital) might have been expected to increase the metal-metal bonding interaction and enhance the stability of the cation. Additionally,

Figure 4.11 The electrochemistry of $Os_2(O_2CC_3H_7)_4Cl_2$ in 0.25 M $TBABF_4/CH_2Cl_2$ at 213 K



attempts to produce these cations by reaction with a variety of chemical oxidants were also unsuccessful. The electrochemical results are interpreted as shown in Equation [23].



...[23]

The products obtained from the reaction of $Os_2(O_2CMe)_4Cl_2$ with a variety of ligands were also investigated using electrochemical techniques. In general the osmium(II) complexes only undergo oxidative processes while the osmium(IV) complexes undergo reductive processes. The osmium(III/III) complex $Os_2(hp)_4Cl_2$ exhibits both types of behaviour. The results of these investigations are summarised below.

$\underline{Os(acac)_2Cl_2}$–

Reversible reduction at $E_{\frac{1}{2}}$ +0.32 V (20 - 200 mVs^{-1} scan rate); irreversible reduction -1.52 V, return wave characteristics develop on cooling to 213 K but never attain full reversibility.

$\underline{Os(S_2CNMe_2)_2Cl_2}$–

Reversible reduction at $E_{\frac{1}{2}}$ -0.54 V (100 - 500 mVs^{-1} scan rate); irreversible reduction at -1.37 V, no improvement on cooling.

$Os_2(hp)_4Cl_2$

Reduction at $E_{\frac{1}{2}}$ +0.26 V (but ΔE_p increases with scan rate, 70 mV at 20 mVs^{-1} to 90 mV at 100 mVs^{-1}, although i_p(anodic)/i_p(cathodic) = 1, at all scan rates); Oxidation at $E_{\frac{1}{2}}$ +1.36 V (but ΔE_p increases with scan rate, 100 mV at 20 mVs^{-1} to 120 mV at 100 mVs^{-1}, i_p(anodic)/ i_p(cathodic) = 1 at all scan rates). Peaks become distended on cooling, consistent with sluggish charge transfer kinetics.

$Os(diphos)_2Cl_2$

Two reversible one-electron oxidations at $E_{\frac{1}{2}}$ +0.38 and +1.60 V (ΔE_p = 60 mV, independent of scan rate and temperature, i_p(anodic)/i_p(cathodic) = 1 at scan rates of 20 - 200 mVs^{-1}).

$[Os_2(diphos)_4Cl_2][BPh_4]_2$

Reversible oxidation at $E_{\frac{1}{2}}$ +1.56 V (at scan rate of 20 - 100 mVs^{-1}); irreversible oxidation at $E_{\frac{1}{2}}$ +1.04 V, characteristic of the $[BPh_4]^-$ anion.

4.6 The electronic spectra of $Os_2(O_2CR)_4Cl_2$ complexes

The electronic spectra of compounds containing metal-metal multiple bonds contain many unusual features. The spectral properties of these complexes are entirely different from those of mononuclear species, and much more complex and rigorous theoretical treatments are required for their interpretation. The majority of work published

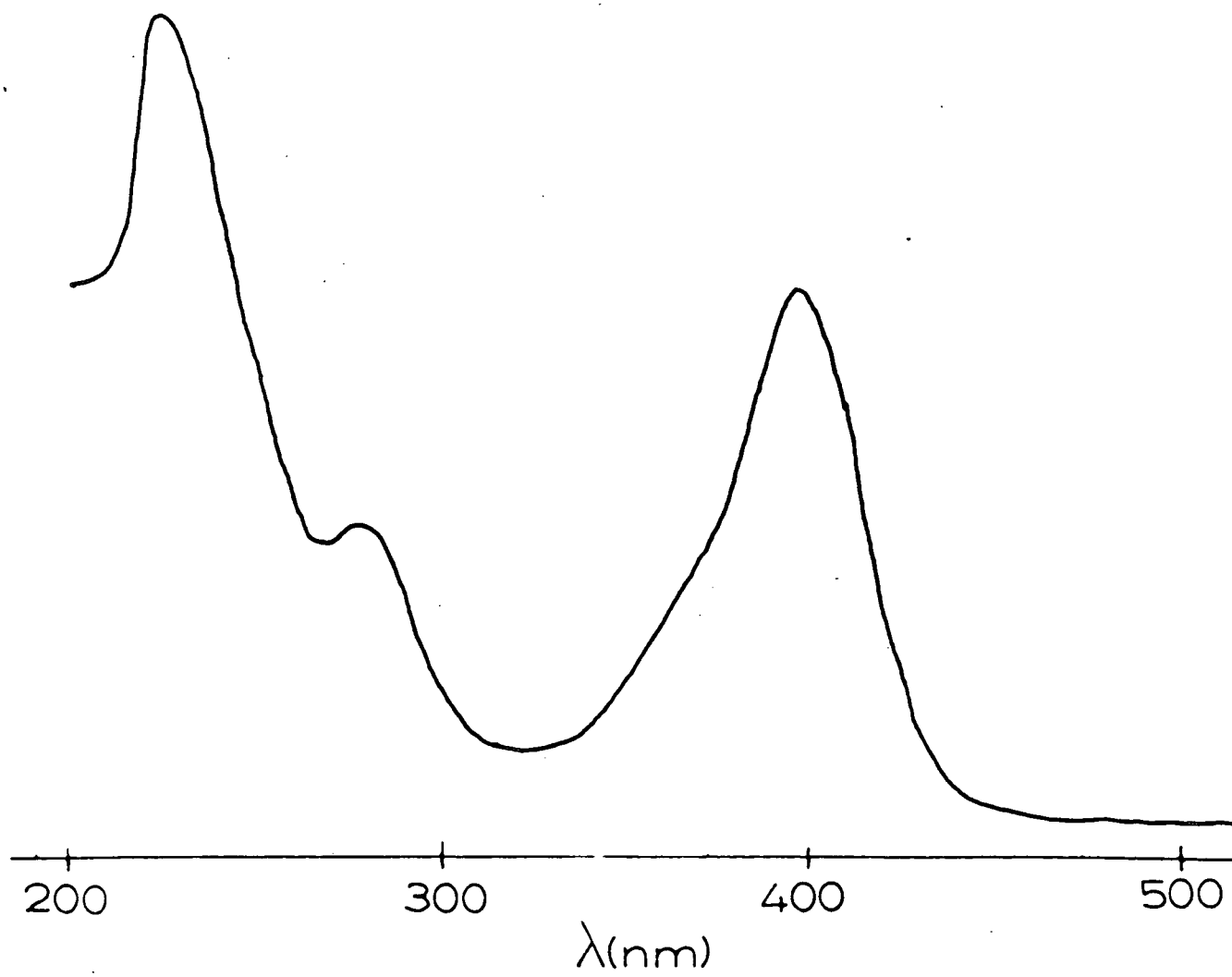
to date has been concerned with species having a $\sigma^2\pi^4\delta^2$ electronic ground state configuration, although some data exists on species with $\sigma^2\pi^4\delta^2\delta^{*m}\pi^{*n}$ configurations. In the case of complexes of the former type, the majority of the effort expended has gone into identifying the $\delta \rightarrow \delta^*$ transitions, which are the lowest energy bands, where the ground state configurations are $\sigma^2\pi^4\delta$, $\sigma^2\pi^4\delta^2$ or $\sigma^2\pi^4\delta^2\delta^*$. Some effort has also been directed towards identifying the nature of the transitions associated with the higher energy bands. To assign these electronic spectra with any degree of certainty it was found necessary to carry out single-crystal studies, between 5K and room temperature, in parallel with theoretical calculations. Few of the studies made to date have been on molecules of the type $M_2(O_2CR)_4$ and $M_2(O_2CR)_4L_2$, although the correct assignment of the $\delta \rightarrow \delta^*$ transition in $Mo_2(O_2CR)_4$ molecules, at ca. 435 nm was achieved after considerable effort[254]. In addition a band at 377 nm has been tentatively assigned to a $\delta \rightarrow \pi^*$ transition.

Recent work has shown that the electronic spectra of $[Ru_2(O_2CR)_4]^+$ cations are quite complex and that definitive assignments are difficult to achieve[223], although earlier solution studies gave relatively simple results that were plausibly assigned[225]. Thus an absorption band at ca. 900 nm was assigned to the $\delta \rightarrow \delta^*$ transition, while the main absorption, at 425 nm, was assigned to an $O(\pi) \rightarrow MM(\pi^*)$ transition, where the "$O(\pi)$" orbital is mainly Ru-O bonding in character, but with an appreciable Ru-Ru π-bonding contribution as well.

Unfortunately, the analysis of the electronic spectra of the osmium carboxylates may prove even more difficult than for the examples discussed above. The principle reason for this is that at ambient temperatures there appears to be an appreciable population of both the ground state electronic configuration, $\sigma^2\pi^4\delta^2\delta^{*2}$, and the first excited state, $\sigma^2\pi^4\delta^2\delta^*\pi^*$ (or $\sigma^2\pi^4\delta^2\pi^{*2}$) (see Section 4.7). Hence electronic transitions from both these states may be possible in the region of the electromagnetic spectrum under investigation (900-200 nm). Solid state reflectance spectra were recorded for R = Me, CH_2Cl while solution data were recorded for R = C_2H_5 and C_3H_7 (see Experimental Section and Figure 4.12). Both sets of spectra are similar with the peaks in the solid state spectrum shifted to higher energy, by ca. 10-20 nm. The peak of lowest energy, at 390 nm, may arise from $\delta^* \rightarrow \pi^*$, $\pi^* \rightarrow \delta^*$ or $\delta \rightarrow \delta^*$ transitions. This peak is however, of medium intensity, ε = 10,400-10,800 $M^{-1}cm^{-1}$, and so is most probably due to the "allowed" $\delta \rightarrow \delta^*$ transition. The weaker absorption, at ca. 280 nm, may be due to one or more of the "forbidden" transitions. The intense band at ca. 220 nm is likely to be associated with charge transfer processes, by comparison with the electronic spectra of other metal-metal multiply bonded complexes.

Obviously a full analysis of these spectra require single-crystal studies over a temperature range coupled with theoretical calculations of the type used by Norman to rationalise the spectrum of $Mo_2(O_2CMe)_4$ [255]. Even then a fully satisfactory analysis will be difficult due to ambiguities arising from the existence of two readily accessible electronic states.

Figure 4.12 The electronic spectrum of $Os_2(O_2C^nC_3H_7)_4Cl_2$ in CH_2Cl_2 between 900-200 nm



4.7 Magnetic and n.m.r. properties of $Os_2(O_2CR)_4Cl_2$

Triple bonds between metal atoms usually arise from the electronic configurations $\sigma^2\pi^4\delta^2\delta^{*2}$, (e.g. Re_2^{4+} derivatives such as $Re_2X_4(PR_3)_4$) or $\sigma^2\pi^4$ (e.g. M_2X_6; M = Mo, W; X = Cl, Br, R, NR_2)[146], in which all the electrons are paired and the complexes are diamagnetic. However, variable temperature magnetic measurements from 300 - 180 K on dichloromethane solutions of the propionate and n-butyrate (by Evans' method[256]) show that these compounds are paramagnetic. However the magnitude of μ_{eff}, (e.g. for R = $n\text{-}C_3H_7$, μ_{eff} decreases from 1.15 BM/Os at 300 K to 1.02 BM/Os at 188 K, and also see Experimental Section), is indicative of considerable antiferromagnetic interaction between osmium(III) ions. In constrast, mer-$Os_2Cl_3(PMe_2Ph)_3$ shows the behaviour expected for a magnetically dilute osmium(III) compound[257], i.e. μ_{eff} = 1.70 BM (almost temperature invariant). Solid state magnetic measurements follow a similar pattern, e.g., for R = Me, μ_{eff} at 288 K is 1.17 BM/Os falling to 0.95 BM/Os at 209 K. It is therefore reasonable to suggest that for these $Os_2(O_2CR)_4Cl_2$ complexes there is an appreciable population of a spin triplet state (perhaps corresponding to the electronic configuration $\sigma^2\pi^4\delta^2\pi^{*2}$ or $\sigma^2\pi^4\delta^{*1}\pi^{*1}$) at ambient temperature with the singlet ground state (arising from the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration) becoming increasingly favoured as the temperature is lowered. In support of this proposal recent SCF-Xα-SW calculations by Norman on $[Ru_2(O_2CH)_4]^+$ and related species indicate an

electronic ground state configuration of $\sigma^2\pi^4\delta^2\pi^{*2}\delta^{*1}$ with a very small energy gap between π^* and δ^* orbitals[225]. The difference in behaviour between complexes containing isoelectronic Mo_2^{2+}, Re_2^{4+} and Os_2^{6+} cores may be due to the higher positive charge on the latter, causing a weakening of the interactions between the metal centres and hence producing a low lying spin triplet level. In support of this, the Re-Re distance in $Re_2Cl_4(PEt_3)_4$ is only 2.232(5) Å[258,259].

Although no e.s.r. signals were observed for these compounds, down to liquid nitrogen temperatures, further evidence for significant amounts of unpaired electron density in these $Os_2(O_2CR)_4Cl_2$ compounds is provided by the occurrence of sharp, contact-shifted resonances in both the ^1H and ^{13}C n.m.r. spectra of $Os_2(O_2C^nC_3H_7)_4Cl_2$ (see Figures 4.13 and 4.14). All the resonances are displaced to lower frequency compared to their position in a diamagnetic environment with the atoms lying closest to the diamagnetic centres (H_B and C_A respectively) experiencing by far the largest shift.

The analysis of the variation of isotropic n.m.r. shifts with temperature, in terms of contact and psuedo contact terms, is complex. This has however, been done successfully for a variety of 2,2'-bipyridyl[260] and acetylacetonate[261] transition metal complexes, where the results of crystal structure determinations are likely to be equally applicable to the structure in solution.

Figure 4.13 The ^{1}H n.m.r. spectrum of $Os_2(O_2C^nC_3H_7)_4Cl_2$ in CD_2Cl_3 at 293 K

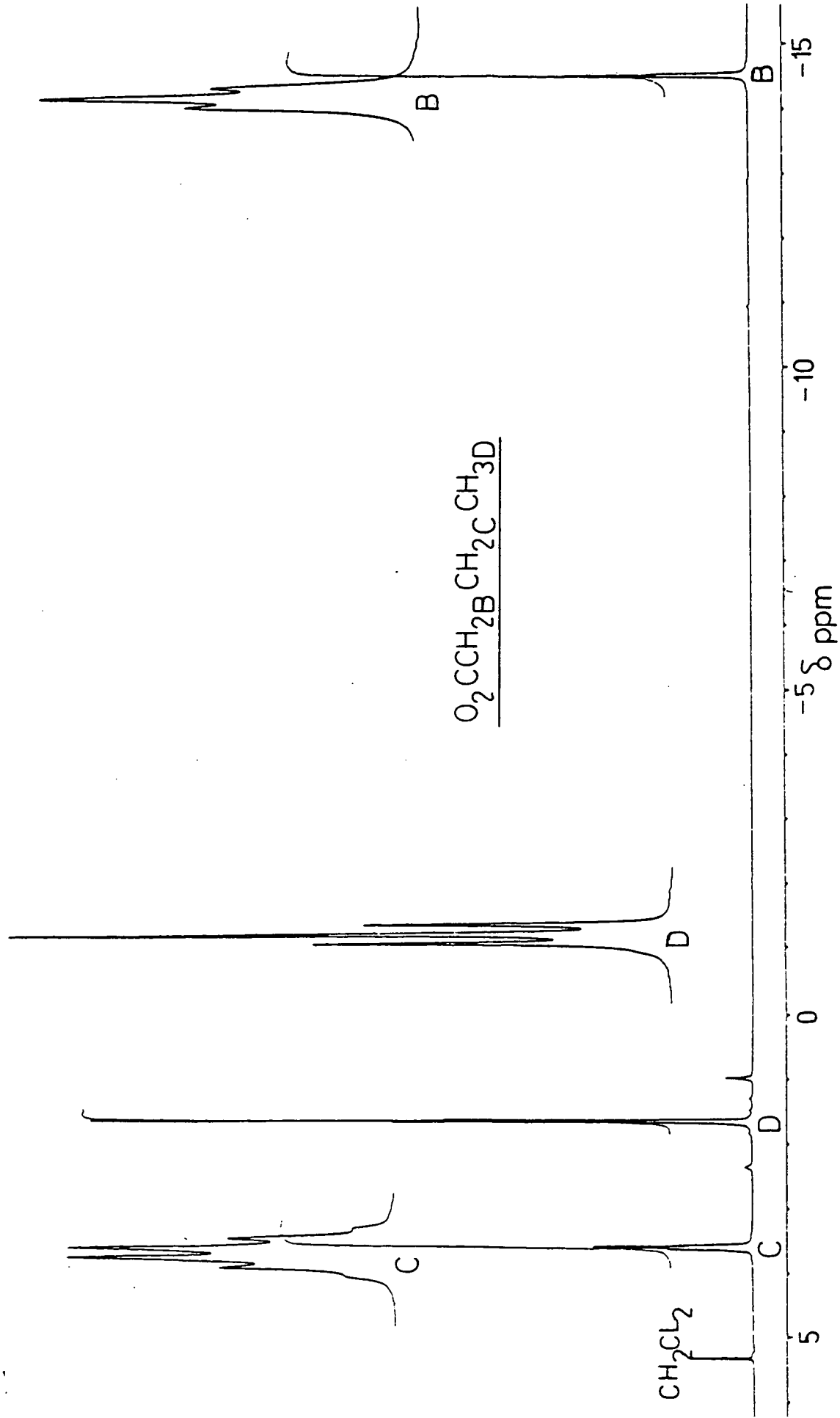
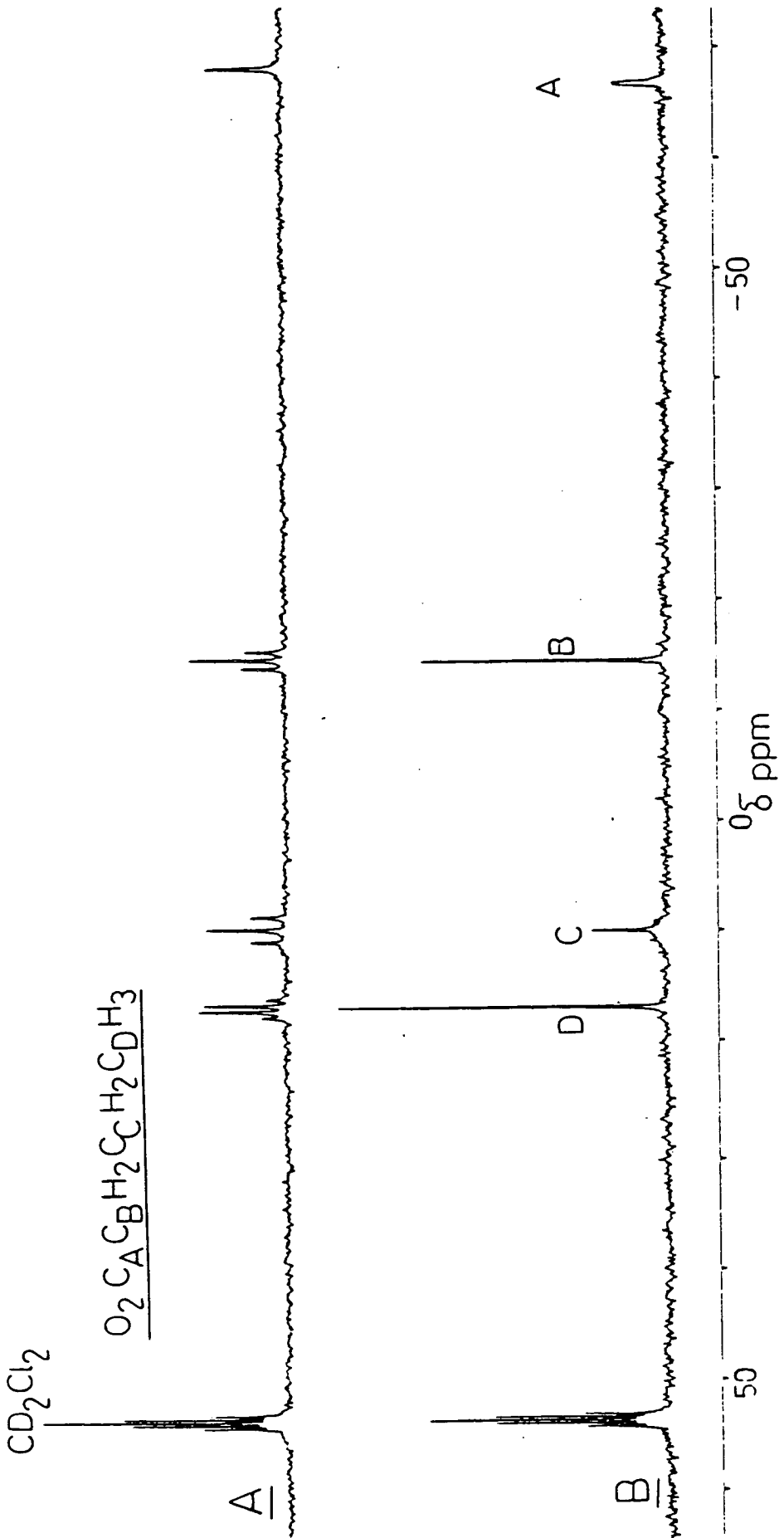


Figure 4.14 The ^{13}C n.m.r. spectrum of $Os_2(O_2C^nC_3H_7)_4Cl_2$ in CD_2Cl_2 at 298 K (A off-resonance : decoupled, B noise decoupled)



Unfortunately, however, this is not likely to be the case for $Os_2(O_2C^nC_3H_7)_4Cl_2$. The geometric parameters of importance are the angle between the atom under consideration and the principal molecular axis, and the distance between that atom and the paramagnetic centre. As the ligand is fluxional in the temperature range available then both vary to a considerable extent. In addition the location of the paramagnetic centre is in doubt, should measurements be made from one of the osmium ions or from the mid-point of the metal-metal bond? The fact that the molecules are distributed statistically over two electronic configurations adds a further complication as the term ΔF, the free energy difference between magnetic states, must be factored into the appropriate equations. Calculations such as this should be possible for complexes with acetate or formate bridging ligands but the low solubility of these species would preclude obtaining n.m.r. spectra of sufficient quality for accurate measurement.

4.8 Experimental

Microanalyses, infrared and n.m.r. spectra, melting point, conductivity measurements and mass spectra were obtained as described in earlier chapters. Electrochemical studies were carried out using the apparatus described in Chapter 3. The electrolyte solution was 0.25 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in CH_2Cl_2. Magnetic measurements were made on a Faraday balance (solid) and in solution by the Evans' method[256] on a Varian Associates HA-100 n.m.r. spectrometer equipped with a variable temperature probe. Electronic spectra were obtained on Pye-Unicam SP8-400 (solution) and Beckman Acta MIV (solid) spectrophotometers. Analytical data for the osmium compounds are given in Table 4.1.

Crystal structure determination of $Os_2(O_2C^nC_3H_7)_4Cl_2$

Crystals suitable for X-ray analysis were obtained by the slow cooling of a solution of the complex in n-butyric acid. A dark green needle shaped crystal (0.35 x 0.18 x 0.04 mm) was used to collect 2100 unique data out to $\theta = 25^{\circ}$ on a Nonius CAD-4 diffractometer with monochromated $M_o - K_\alpha$ radiation.

Crystal data: $Os_2Cl_2C_{16}H_{28}O_8$, M = 799, a = 6.789(2), b = 11.790(1), c = 14.923(1) Å, $\beta = 98.211(18)^{\circ}$, V = 1182 Å^3, Z = 2, $D_c = 2.25$ g cm^{-3}, F(000) = 748, $\lambda = 0.71069$ Å, $\mu(M_o - K_\alpha) = 116.8$ cm^{-1}. The space group is $P2_1/n$.

Structure solution and refinement

The structure was solved by conventional Patterson and difference Fourier techniques. The position of the osmium atom was determined from a Patterson map. Subsequent difference-Fourier synthesis revealed all non-hydrogen atoms in the molecule. The structure refinement was carried out using SHELX[74]. In the final cycles of least squares refinement Os, O, C, Cl were given anisotropic vibrational parameters. No hydrogen atoms were included in the refinement. The weighting scheme $w = 1.0/[\sigma^2(F) + 0.00089\ F^2]$ was applied. The final R factor was 0.044 based on 1686 reflections with $I > 2.5\sigma(I)$.

Figure 4.5 shows the geometry of the molecule and Figure 4.6 a cell packing diagram. No short intermolecular contacts were observed. Table 4.2 gives the final fractional coordinates and selected bond distances and angles are presented in Table 4.3.

Tetra-μ-acetatodichlorodiosmium(III)

Sodium hexachloroosmate (1.0 g, 2.2 mmol), acetic acid (35 ml), acetic anhydride (15 ml) and concentrated hydrochloric acid (2 ml) were refluxed for 6-8 hours. The mixture was then filtered and the product washed with water, methanol and diethylether and dried *in vacuo* at 56°C. Refluxing the filtrate for a further 6-8 hours gave a second sample of the product. Total yield *ca.* 550 mg, 72% m.p. 273-275°C. Infrared spectrum $\nu(CO_2)_{asym}$ 1450 cm^{-1}, $\nu(CO_2)_{sym}$ 1380 cm^{-1} $\Delta(\nu_{asym} - \nu_{sym})$ = 70 cm^{-1}: Mass spectrum; m/e 687, $[Os_2(O_2CMe)_4Cl_2]^+$;652, $[Os_2(O_2CMe)_4Cl]^+$;

617, $[Os(O_2CMe)_4]^+$. Magnetic moment (solid); μ_{eff} 1.17 BM/Os (288 K) to 0.95 BM/Os (209 K). Electronic spectrum (200 - 900 nm, solid state reflectance): 260 nm (br), 370(br).

Tetra-μ-propionatodichlorodiosmium(III)

The compound $Os_2(O_2CMe)_4Cl_2$ (0.12 g, 0.17 mmol) was heated in propionic acid (15 ml) at ca. 140°C for 5 hours, then cooled to yield a dark green solid which was collected, washed with methanol and diethylether and dried in vacuo at 56°C. Yield 30 mg, 23%, m.p. 238-240°C. The compound is soluble in CH_2Cl_2 and sparingly soluble in $(CH_3)_2CO$. IR: $\nu(CO_2)_{asym}$ 1478 cm^{-1}, $\nu(CO_2)_{sym}$ 1375 cm^{-1}, $\Delta(\nu_{asym} - \nu_{sym})$ = 103 cm^{-1}. Mass spectrum: m/e 743, $[Os_2(O_2CC_2H_5)_4Cl_2]^+$; 708, $[Os_2(O_2CC_2H_5)_4Cl]^+$; 673, $[Os_2(O_2CC_2H_5)_4]^+$. Magnetic moment in CH_2Cl_2, μ_{eff} 1.13 BM/Os (300 K) to 1.02 BM/Os (188 K) (Curie-Weies constant θ = -173 K). Electronic spectrum (200 - 900 nm) in CH_2Cl_2: 222 nm (ε = 15,600), 244(sh), 277(s,800), 364(sh), 392(10,800).

Tetra-μ-n-butyratodichlorodiosmium(III)

The compound was prepared as above from $Os_2(O_2CMe)_4Cl_2$ and n-butyric acid. Yield 57%, m.p. 169-171°C. The compound is soluble in CH_2Cl_2, C_6H_6 and $(CH_3)_2CO$. M(C_6H_6), osmometrically 832, (1.2 x 10^{-3} M), 786, (0.85 x 10^{-3} M); 777, (0.51 x 10^{-3} M); required 799. IR: $\nu(CO_2)_{asym}$ 1471 cm^{-1}; $\nu(CO_2)_{sym}$ 1358 cm^{-1}; $\Delta(\nu_{asym} - \nu_{sym})$ = 113 cm^{-1}.

Mass spectrum: m/e 799, $[Os_2(O_2CC_3H_7)_4Cl_2]^+$; 764, $[Os_2(O_2CC_3H_7)_4Cl]^+$; 729, $[Os_2(O_2CC_3H_7)_4]^+$.
Magnetic moment in CH_2Cl_2, μ_{eff} 1.15 BM/Os (300 K) to 1.02 BM/Os (188 K) (Curie-Weiss constant θ = -206 K).
Electronic spectrum (200-900 nm) in CH_2Cl_2: 233 nm (ε = 15,800), 260(sh), 278(6,100), 360(sh), 392(10,400).

Tetra-μ-monochloroacetatodichlorodiosmium(III)

The compound $Os_2(O_2CMe)_4Cl_2$ (0.11 g, 0.16 mmol) was heated with an excess of molten monochloroacetic acid (8 g) at 120°C for 3 hours. The cooled solid was washed copiously with diethylether and the green micro-crystalline residue dried in vacuo at 56°C. Yield 60 mg, 45%, m.p. 251-253°C. The compound rapidly decomposes in CH_2Cl_2 and is insoluble in other solvents. IR: $\nu(CO_2)_{asym}$ 1467 cm^{-1}; $\nu(CO_2)_{sym}$ 1388 cm^{-1}, $\Delta(\nu_{asym} - \nu_{sym})$ = 79 cm^{-1}.
Mass spectrum: m/e 825, $[Os_2(O_2CCH_2Cl)_4Cl_2]^+$; 790, $[Os_2(O_2CCH_2Cl)_4Cl]^+$; 755, $[Os_2(O_2CCH_2Cl)_4]^+$.
Electronic spectrum (200-900 nm, solid state reflectance): 260(br), 357(br).

Reactions of the acetate

Tetra-μ-2-hydroxopyridinatodichlorodiosmium(III)

The compound $Os_2(O_2CMe)_4Cl_2$ (0.10 g, 0.14 mmol) was refluxed in methanol (30 ml) containing an excess of 2-hydroxypyridine (1.0 g) for 3 hours after which the volume was reduced to 20 ml and the resulting dark red-purple solid collected and washed with methanol and diethylether and dried in vacuo. Yield 60 mg, 51%, m.p. >250°C. The compound is soluble in CH_2Cl_2, $(CH_3)_2CO$ and

and CH_3CN. Mass spectrum: m/e 827, $[Os_2(hp)_4Cl_2]^+$; 792, $[Os_2(hp)_4Cl]^+$; 757, $[Os_2(hp)_4]^+$. Magnetic moment in CH_2Cl_2: μ_{eff} 1.44 BM/Os (300 K) to 1.22 BM/Os (195 K). Electronic spectrum (200-900 nm) in CH_2Cl_2: 222 nm (ε = 27,000); 282 (16,100); 488 (5,700).

Trans-bis(acetylacetonato)dichloroosmium(IV)

The compound $Os_2(O_2CMe)_4Cl_2$ (0.10 g, 0.14 mmol) was refluxed in acetylacetone (5 ml) for 6 hours to give a dark red solution which deposits on cooling a small amount of microcrystalline red solid which was collected, washed with methanol and diethylether and dried in vacuo. Yield 10 mg, 15%, m.p. 268-270°C (decomp.). The compound is slightly soluble in CH_2Cl_2. IR: ν(Os-Cl) 340 cm^{-1}. Mass spectrum: m/e 459, $[Os(acac)_2Cl_2]^+$; 424, $[Os(acac)_2Cl]^+$. Magnetic moment (solid state): μ_{eff} = 1.29 BM (288 K). Electronic spectrum (200-900 nm) in CH_2Cl_2: 275 (ε = 11,600): 343 (6,700): 362(sh); 544(2,600).

Tetra-μ-2,2,2-trifluoroacetamidodichlorodiosmium(III)

The compound $Os_2(O_2C^nC_3H_7)_4Cl_2$ (0.10 g, 0.13 mmol) was heated in an excess of 2,2,2-trifluoroacetamide (3.0 g) at 110°C for 1.5 hours. The cooled melt was washed with diethylether to remove the trifluoroacetamide and methylene chloride to remove any unreacted osmium butyrate. The orange-brown product was then dried in vacuo. Yield 20 mg, 8%, m.p. >270°C. The compound is insoluble in all common solvents.

Triphenylbenzylphosphonium hexachloroosmate(IV)

The acetate, $Os_2(O_2CMe)_4Cl_2$, (0.15 g, 0.22 mmol) was warmed in hydrochloric acid (20 ml, 18 M) to give a yellow solution. Addition of $[Ph_3(PhCH_2)P]Cl$ then led to the slow precipitation of the crystalline $[Ph_3(PCH_2)P]_2[OsCl_6]$ which was collected, washed with water, methanol and diethylether and dried in vacuo at 56°C. Yield 310 mg, 64%. The same compound was prepared by treating an aqueous solution of $Na_2[OsCl_6]$ with $[Ph_3(PhCH_2)P]Cl$. Electrochemistry (293 K): -0.54 V (one electron reversible reduction), -1.62 V (irreversible reduction), +1.40 V (one electron reversible oxidation).

Triphenylbenzylphosphonium hexabromoosmate(IV)

The compound, $Os_2(O_2CMe)_4Cl_2$, (0.10 g, 0.14 mmol) was stirred with warming in concentrated hydrobromic acid (15 ml, 48%) containing KBr (1.0 g) to give a deep red solution. After addition of $[Ph_3(PhCH_2)P]Cl$ the product was extracted with methylene bromide. This was evaporated to dryness and the solid recrystallised from methanol. Yield 140 mg, 35%. Electrochemistry (293 K): -0.32 V (one electron reversible reduction), -1.70 V (irreversible reduction), +1.40 V (one electron reversible oxidation).

Tris(N,N-bipyridyl)osmium(II)tetraphenylborate

The compound, $Os_2(O_2CMe)_4Cl_2$, (0.12 g, 0.17 mmol) was refluxed with an excess of 2,2'-bipyridyl (1.0 g) in methanol (25 ml) for 3 hours to give a dark green solution. This was then filtered, $Na[BPh_4]$ (0.3 g) added and the precipitated green solid collected, washed with methanol and then recrystallised from CH_2Cl_2. Yield 250 mg, 56%. Electrochemistry (293 K): reversible one electron reductions at -1.05, -1.31, -1.64 V; irreversible oxidation at +1.06 V.

Similarly prepared was $[Os(1,10\text{-phen})_3][BPh_4]_2$.

Bis(N,N-dimethyldithiocarbamato)dichloroosmium(IV)

The acetate, $Os_2(O_2CMe)_4Cl_2$, (0.15 g, 0.21 mmol) was refluxed with an aqueous solution of $Na[S_2CNMe_2].3H_2O$ (0.55 g, 2.5 mmol in 15 ml H_2O) for 6 hours. The dark red powder formed was collected, washed with water, ethanol and diethylether and then dried in vacuo. Yield 20 mg, 18%, m.p. >250°C.

Bis(1,2-bis(diphenylphosphino)ethane)dichloroosmium(II)

The compound $Os_2(O_2CMe)_4Cl_2$ (0.15 g, 0.22 mmol) was refluxed with $Ph_2P(CH_2)_2PPh_2$ (1.0 g) in methanol (20 ml) for 4 hours. The solution was cooled and the pale yellow solid filtered off, washed with methanol and diethylether and then dried in vacuo. Yield 40 mg, 9%, m.p. >275°C.

IR: ν(Os-Cl) 343 cm^{-1}. Mass spectrum: m/e 1057, $[Os(diphos)_2Cl_2]^+$; 1022, $[Os(diphos)_2Cl]^+$; 987, $[Os(diphos)_2]^+$. $^{31}P-\{^1H\}$ n.m.r. in CD_2Cl_2 at 301 K: δ7.3(s) ppm. The compound is sparingly soluble in CH_2Cl_2.

Addition of $Na[BPh_4]$ (0.40 g) to the dark grey filtrate gave a blue-grey precipitate of $[Os_2Cl_2(diphos)_4][BPh_4]_2$, which was collected washed with methanol, and dried in vacuo. Yield 180 mg, 31%, m.p. 171°C (decomp.). $^{31}P-\{^1H\}$ n.m.r. in CD_2Cl_2 at 301 K: δ ppm 36.5(t); 5.5(t), $^2J_{P-P}$ 4.40 Hz. Conductivity in CH_3NO_2 at 303 K: slope of $\Lambda_o - \Lambda_e$ vs. $C_e^{\frac{1}{2}}$ plot = 735 (typical of 1:2 electrolyte). The compound is also soluble in acetone.

Table 4.1 Analytical data[a] for some osmium compounds

	%C	&H	%other
$Os_2(O_2CMe)_4Cl_2$	14.1(14.0)	1.7(1.7)	10.5(10.3)[b]
$Os_2(O_2CC_2H_5)_4Cl_2$	19.2(19.4)	2.7(2.7)	9.6(9.6)[b]
$Os_2(O_2C^nC_3H_7)_4Cl_2$	24.2(24.0)	3.5(3.5)	9.0(8.9)[b]
$Os_2(O_2CCH_2Cl)_4Cl_2$	11.7(11.5)	1.0(1.0)	23.2(25.5)[b]
$Os(acac)_2Cl_2$	26.5(26.1)	2.9(3.1)	15.0(15.5)[b]
$Os_2(ONHCCF_3)_4Cl_2$	10.9(10.7)	0.6(0.6)	6.0(6.2)[c]
$Os(SCNMe)_2Cl_2$	15.6(14.4)	2.5(2.4)	5.8(5.6)[c]
$Os(diphos)_2Cl_2$	60.8(59.9)	4.6(4.6)	-
$[Os_2Cl_2(diphos)_4][BPh_4]_2$	66.5(68.0)	5.1(5.1)	-
$[Os(2,2'\text{-bipy})_3][BPh_4]_2$	71.9(72.2)	4.8(5.0)	6.4(6.5)[c]
$Os_2(hp)_4Cl_2$	28.0(29.0)	1.9(2.0)	6.7(6.8)[c]
$[Ph_3(PhCH_2)P]_2[OsCl_6]$	53.7(54.1)	3.9(4.0)	-
$[Ph_3(PhCH_2)P]_2[OsBr_6]$	43.7(43.6)	3.3(3.2)	-

(a) Calculated values in parenthesis
(b) Chloride analysis
(c) Nitrogen analysis

Table 4.2 Fractional coordinates for $Os_2(O_2C^nC_3H_7)_4Cl_2$

	X	Y	Z
Os	0.08828(6)	0.44036(4)	0.45944(3)
Cl(1)	0.2845(6)	0.3171(3)	0.3776(3)
O(1)	-0.1208(12)	0.4622(7)	0.3504(6)
O(2)	-0.2921(12)	0.5767(6)	0.4292(6)
C(1)	-0.2664(18)	0.5238(10)	0.3565(8)
C(2)	-0.4205(20)	0.5423(13)	0.2736(10)
C(3)	-0.3295(28)	0.5942(19)	0.1989(12)
C(4)	-0.2152(30)	0.6979(16)	0.2219(15)
O(3)	0.2344(13)	0.5736(6)	0.4192(6)
O(4)	-0.0672(12)	0.3092(6)	0.5015(6)
C(5)	0.1977(18)	0.6709(11)	0.4461(9)
C(6)	0.3123(20)	0.7659(11)	0.4113(12)
C(7)	0.2366(23)	0.8809(14)	0.4287(13)
C(8)	0.3576(27)	0.9675(14)	0.3840(13)

Table 4.3 Selected bond distances and angles for $Os_2(O_2C^nC_3H_7)_4Cl_2$

Bond lengths (Å)

Os-Os	2.301(1)
Os-Cl(1)	2.417(3)
Os-O(1)	2.018(8)
Os*-O(2)	2.015(8)
C(1)-O(1)	1.241(14)
C(1)-O(2)	1.284(15)
C(1)-C(2)	1.518(25)
C(2)-C(3)	1.482(21)
C(3)-C(4)	1.462(26)
Os-O(3)	1.996(7)
Os*-O(4)	2.022(8)
C(5)-O(3)	1.252(14)
C(5)-O(4)	1.284(15)
C(5)-C(6)	1.499(18)
C(6)-C(7)	1.486(21)
C(7)-C(8)	1.523(25)

Bond angles (°)

Cl(1)-Os-Os*	177.96(10)
O(1)-Os-Os*	89.27(23)
O(2)-Os-Os*	88.55(23)
O(3)-Os-Os*	89.79(24)
O(4)-Os-Os*	88.23(23)
Os-O(1)-C(1)	119.41(8)
O(1)-C(1)-O(2)	119.41(8)
O(1)-C(1)-O(2)	123.5(10)
C(1)-O(2)-Os*	119.2(7)
Os-O(3)-C(5)	119.6(8)
O(3)-C(5)-O(4)	123.3(11)
C(5)-O(4)-Os*	119.04(8)

* represents the atom related by $\bar{x}$, $\bar{y}$, $\bar{z}$.

APPENDIX I

The X-Ray Structural Analysis of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$

A.1 Introduction

During the preparation of this thesis the crystal structure of $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$ was determined. This was deemed necessary in view of the fact that no tri-μ-hydroxo-η-benzeneruthenium(II) binuclear complex had ever been unequivocally identified, although several tetranuclear complexes had been identified and the analogous η-mesitylene complex had been shown to be binuclear (see Chapter 2). It was therefore of some importance to determine the nature of the alkoxo complexes derived from these tetranuclear precursors. The results of this determination, as shown below, constitute the first crystallographic study of a binuclear complex containing bridging methoxo ligands, in the chemistry of the platinum metals.

A.2 Results and Discussion

The crystal structure determination confirms the binuclear nature of the tri-μ-methoxo bridged complexes. The Ru-Ru distance of 3.005(2) Å is of similar magnitude to that found for the hydroxyl bridged complexes. The Ru-O distances lie between 2.044 and 2.080 Å and have an average value of 2.060(8) Å. Although bonds to O(3) are longer the difference does not appear to be significant. The Ru-C distances for the two rings are 2.155(14) and 2.158(13) Å while the distance from the metal to the ring centroids are 1.643 and 1.646 Å respectively. The two benzene rings are staggered with respect to each other (see Figure A.1)

Figure A.1 The molecular structure of the cation $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$

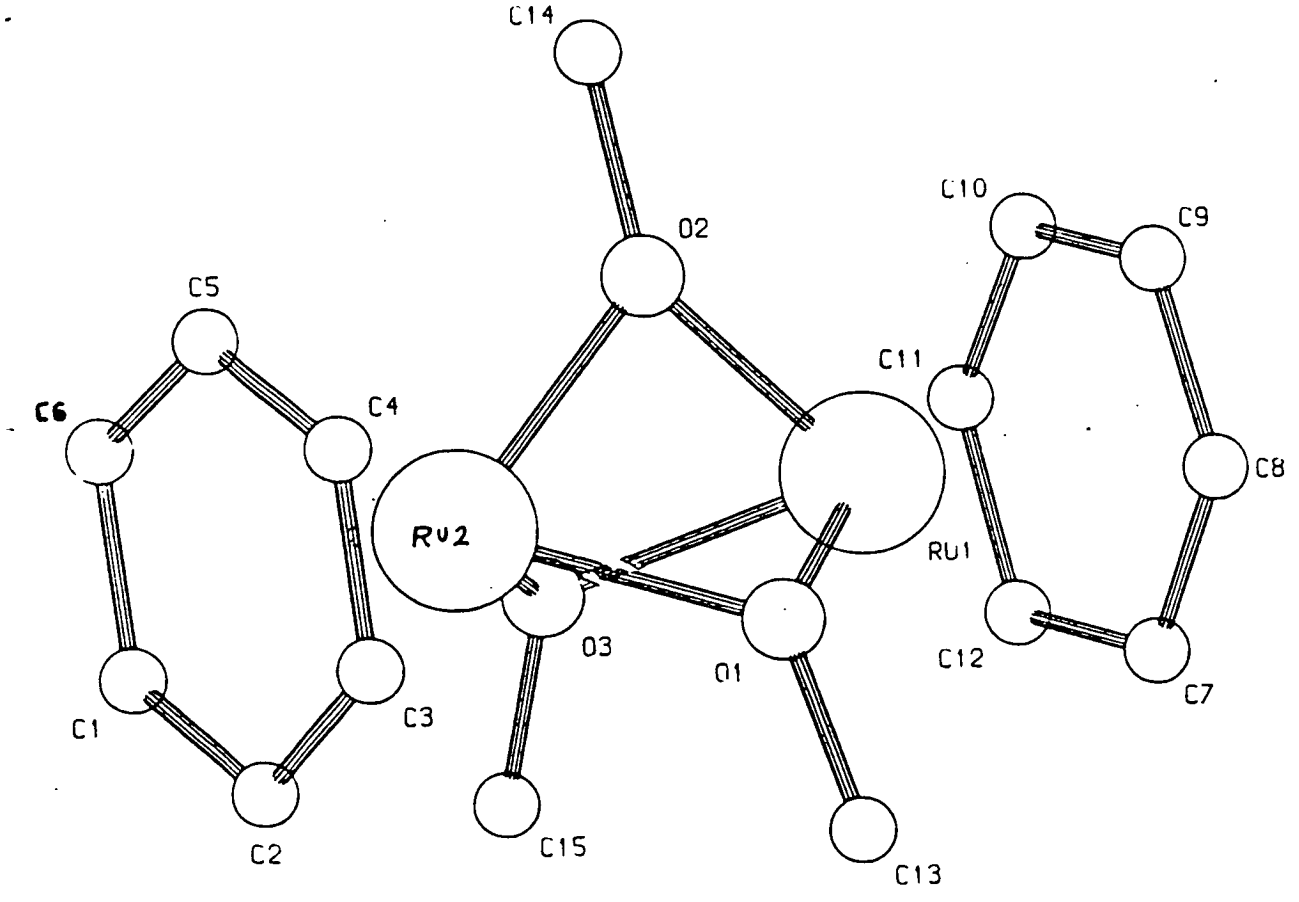
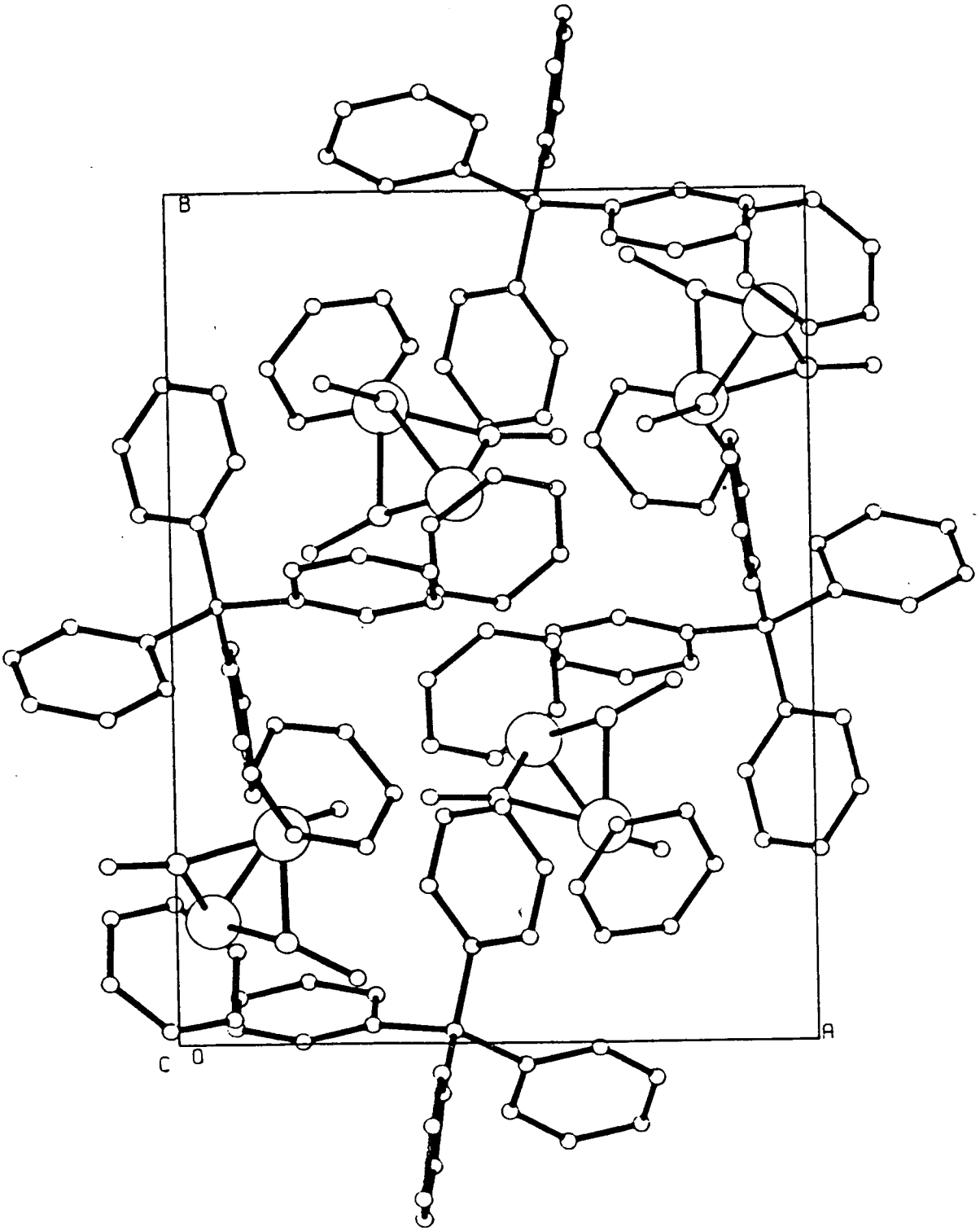


Figure A.2 A cell packing diagram for $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$



and disordered over two positions (see below). The Ru-O-Ru angles lie in the range 92.6 to 94.6° and the O-Ru-O angles in the range 71.4 - 74.9° (see Table A.2). These values are very similar to those found in the hydroxo bridged compound $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2.2Me_2CO$. The structure of the cation is shown in Figure A.1 and a cell packing diagram in Figure A.2.

A.3 Experimental

Crystals suitable for X-ray analysis were obtained by the slow cooling of a methanolic solution of the complex to 273 K for 24 hours. A yellow needle crystal (0.2 x 0.1 x 0.1 mm) was mounted along the needle axis and the data collected in the ω-2θ scan mode using a CAD-4 diffractometer with monochromated M_o - K_α radiation for θ out to 25°.

Crystal Data: $Ru_2C_{39}H_{41}BO_3$, M = 771, monoclinic
$\underline{a}$ = 11.725(4), $\underline{b}$ = 15.573(5), $\underline{c}$ = 18.739(2), β = 103.29(2)
$D\underline{c}$ = 1.53 g cm^{-3}, $D\underline{m}$ = 1.51 g cm^{-3} (by flotation),
z = 4, $\mu(M_o - K_\alpha)$ = 9.15 cm^{-1}, $\lambda(M_o - K_\alpha)$ = 0.71069 Å.
The space group is $P2_1/n$.

Intensities were measured for 4349 unique reflections of which 2546 had I > 2.5 (I). No crystal decay was observed and no absorption correction applied.

Structure Solution and Refinement

The two ruthenium atoms were located using SHELX-84[262] and all remaining non-hydrogen atoms were found from subsequent Fourier maps. The ruthenium and oxygen atoms were refined anisotropically. In the refinement both the benzene rings and the phenyl groups of the tetraphenylborate were constrained to be regular hexagons. The benzene rings were disordered over two positions. In the refinement each set of six carbon atoms were given individual site occupancy factors and thermal parameters. In the latter stages of refinement hydrogen atoms were included in fixed positions to give C-H = 1.10 Å, with a fixed common temperature factor of U = 0.08 Å^2. The hydrogen atoms of the o-methyl ligands were located from the Fourier map and refined with a common temperature factor. The weighting scheme applied was $W = 1/\sigma^2(F_o) + 0.0014\ F_o^2]$ and the final R factor was R = 0.052, R_w = 0.064. A final difference map showed three peaks each of about $^3/4\ e$Å^{-3} which occurred near the bridging oxygen, O(5), and the disordered benzene rings. Final fractional coordinates are given in Table A.1 and selected bond distances and angles in Table A.2.

Table A.1 Fractional Coordinates for $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3][BPh_4]$

Cation	X	Y	Z
Ru(1)	0.44249(8)	0.64469(6)	0.57108(4)
Ru(2)	0.33189(7)	0.74695(6)	0.43696(4)
O(1)	0.3412(6)	0.7534(4)	0.5478(3)
O(2)	0.4971(6)	0.7125(6)	0.4915(4)
O(3)	0.3282(7)	0.6199(4)	0.4708(3)
C(1)	0.2034(14)	0.7337(6)	0.3350(7)
C(2)	0.1610(14)	0.7904(6)	0.3804(7)
C(3)	0.2278(14)	0.8614(6)	0.4102(7)
C(4)	0.3370(14)	0.8756(6)	0.3946(7)
C(5)	0.3793(14)	0.8189(6)	0.3491(7)
C(6)	0.3125(14)	0.7480(6)	0.3193(7)
C(7)	0.4107(11)	0.6096(9)	0.6748(7)
C(8)	0.5063(11)	0.6653(9)	0.6864(7)
C(9)	0.6020(11)	0.6467(9)	0.6565(7)
C(19)	0.6020(11)	0.5723(9)	0.6150(7)
C(11)	0.5064(11)	0.5166(9)	0.6034(7)
C(12)	0.4107(11)	0.5352(9)	0.6333(7)
C(13)	0.2458(16)	0.7761(10)	0.5797(8)
C(14)	0.6026(15)	0.7125(11)	0.4686(8)
C(15)	0.2179(14)	0.5787(9)	0.4661(8)
Tetraphenylborate			
B(1)	0.0732(11)	0.5149(7)	0.7541(6)
C(16)	0.0427(6)	0.6135(3)	0.7168(3)
C(17)	-0.0471(6)	0.6241(3)	0.6542(3)
C(18)	-0.0725(6)	0.7056(3)	0.6238(3)
C(19)	-0.0082(6)	0.7765(3)	0.6561(3)
C(20)	0.0816(6)	0.7660(3)	0.7188(3)
C(21)	0.1070(6)	0.6844(3)	0.7491(3)
C(22)	0.1972(5)	0.5211(4)	0.8213(3)
C(23)	0.1918(5)	0.5558(4)	0.8892(3)
C(24)	0.2948(5)	0.5720(4)	0.9417(3)

Table A.1 (contd.)

C(25)	0.4032(5)	0.5537(4)	0.9264(3)
C(26)	0.4086(5)	0.5191(4)	0.8586(3)
C(27)	0.3056(5)	0.5028(4)	0.8061(3)
C(28)	0.0935(6)	0.4414(4)	0.6908(3)
C(29)	0.0925(6)	0.4643(4)	0.6187(3)
C(30)	0.1073(6)	0.4016(4)	0.5684(3)
C(31)	0.1232(6)	0.3159(4)	0.5903(3)
C(32)	0.1241(6)	0.2930(4)	0.6624(3)
C(33)	0.1093(6)	0.3558(4)	0.7126(3)
C(34)	-0.0368(5)	0.4744(4)	0.7902(4)
C(35)	-0.1535(5)	0.4935(4)	0.7580(4)
C(36)	-0.2431(5)	0.4578(4)	0.7861(4)
C(37)	-0.2160(5)	0.4030(4)	0.8465(4)
C(38)	-0.0993(5)	0.3839(4)	0.8788(4)
C(39)	-0.0097(5)	0.4196(4)	0.8507(4)

Table A.2 Selected bond distances and angles for the cation $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]^+$

(a) Bond lengths (Å) with standard deviation ( )

Ru(1)-Ru(2)	3.005(2)	Ru(2)-O(1)	2.057(7)
Ru(1)-O(1)	2.056(7)	Ru(2)-O(2)	2.044(8)
Ru(1)-O(2)	2.046(8)	Ru(2)-O(3)	2.080(7)
Ru(1)-O(3)	2.078(7)	Ru(2)-C(1)	2.154(13)
Ru(1)-C(7)	2.133(14)	Ru(2)-C(2)	2.149(13)
Ru(1)-C(8)	2.142(14)	Ru(2)-C(3)	2.153(13)
Ru(1)-C(9)	2.164(14)	Ru(2)-C(4)	2.162(13)
Ru(1)-C(10)	2.177(14)	Ru(2)-C(5)	2.167(13)
Ru(1)-C(11)	2.168(14)	Ru(2)-C(6)	2.163(13)
Ru(1)-C(12)	2.146(14)		

(b) Bond angles (°) with standard deviation ( )

Ru(1)-O(1)-Ru(2)	93.9(3)	O(2)-Ru(2)-O(3)	71.4(3)
Ru(1)-O(2)-Ru(2)	94.6(3)	Ru(1)-O(1)-C(13)	125.7(8)
Ru(1)-O(3)-Ru(2)	92.6(3)	Ru(1)-O(2)-C(14)	132.1(8)
O(1)-Ru(1)-O(2)	71.5(3)	Ru(1)-O(3)-C(15)	121.7(8)
O(1)-Ru(1)-O(3)	74.9(3)	Ru(2)-O(1)-C(13)	124.7(8)
O(2)-Ru(1)-O(3)	71.4(3)	Ru(2)-O(2)-C(14)	130.5(8)
O(1)-Ru(2)-O(2)	71.5(3)	Ru(2)-O(3)-C(15)	119.3(7)
O(1)-Ru(2)-O(3)	74.9(3)		

Appendix II - Abbreviations

acac	acetylacetone
bipy	bipyridine
B.M.	Bohr Magneton
Bu	butyl
diphos	Bis(1,2-diphenylphosphino)ethane
en	ethylenediamine
Et	ethyl
e.s.r.	electron spin resonance
Hhp	2-hydroxypyridine
Hmhp	2-hydroxy-6-methylpyridine
Hz	Hertz
Me	methyl
m.p.	melting point
n.m.r.	nuclear magnetic resonance
p-cymene	2-methyl-5-isopropylbenzene
Ph	phenyl
phen	1,10-phenonthroline
p.p.m.	parts per million
Pr	propyl
pyz	pyrazine
T.M.S.	tetramethylsilane

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"Homogeneous Catalysis"

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Tri-μ-chloro-bis[(η-*p*-cymene)ruthenium(II)] Tetraphenylborate Methanol Solvate

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Abstract. $[Ru_2Cl_3\{p\text{-}CH_3.C_6H_4.CH(CH_3)_2\}_2]BPh_4.MeOH$, $C_{44}H_{48}BCl_3Ru_2.CH_3OH$, $M_r = 928$, monoclinic, $I2$ (non-standard setting of $C2$), $a = 27{\cdot}331$ (5), $b = 9{\cdot}765$ (5), $c = 16{\cdot}923$ (2) Å, $\beta = 112{\cdot}748$ (14)°, $U = 4165$ Å^3, $D_m = 1{\cdot}46$, $D_c = 1{\cdot}48$ g cm^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 9·3 cm^{-1}. $R = 0{\cdot}064$ for 2783 observed data with $I > 2{\cdot}5\sigma(I)$. There are two crystallographically independent Ru–Ru dimers each lying across a twofold rotation axis. Ru and Cl atoms were refined anisotropically, all benzene rings were constrained to have ideal geometries. Both Ru···Ru distances are 3·283 Å; Ru···Cl distances lie between 2·41 and 2·45 Å with Ru–Cl–Ru angles in the range 84·1 to 86·1°.

Introduction. The title compound was prepared during studies of binuclear triply bridged arene ruthenium(II) complexes (Arthur & Stephenson, 1981). A number of binuclear triply bridged ruthenium compounds have been examined by X-ray crystallography (Laing & Pope, 1976) and show Ru···Ru distances between 3·44 and 3·08 Å depending on the oxidation state of the Ru atoms and also the nature of the bridging ligands. NMR studies indicated a binuclear diamagnetic complex in which bridging ligands were Cl and terminal ligands π-bonded arenes with both Ru atoms in oxidation state (II). This structure determination is the first to show the nature of the binuclear Ru^{II}–π-arene interaction.

Experimental. Dark-red needles were grown from a 313–333 K petroleum ether–methylene chloride mixture. Preliminary photography showed that the space group was $I2$ or $I2/m$ (alternative settings for $C2$ and $C2/m$; the symmetry operators for $I2$ are x,y,z; $\bar{x},y,\bar{z}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$). A crystal of dimensions 0·15 × 0·15 × 0·25 (needle) mm was mounted along the needle axis. Data were collected in the ω–2θ scan mode using a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation for θ out to 25°. Of the 3869 unique reflections measured, 2783 had $I > 2{\cdot}5\sigma(I)$. No crystal decay was observed and no absorption correction was applied. The two Ru atoms were located from a Patterson map and all remaining non-H atoms were found from subsequent Fourier maps. The structure consists of two crystallographically unrelated dimers. Each Ru···Ru bond is bisected by a twofold rotation axis which also runs through one of the bridging chlorides. One of these molecules was found to show a significant oscillation about the Ru···Ru axis. Disorder was also apparent in one of the phenyl rings of the tetraphenylborate anion and also in the position of the methanol solvent

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molecule. Smooth convergence of this partially disordered structure was facilitated using a constrained least-squares refinement in which all phenyl groups were input as idealized planar rings with C–C bond lengths of 1·395 Å. All other C–C bonds were constrained to 1·54 Å with a weight of 0·01 (*SHELX*, Sheldrick, 1976). H atoms bonded to phenyl groups were included in their calculated positions with a common fixed temperature factor of $U = 0{\cdot}08$ Å^2. In the final cycles of refinement the two independent Ru atoms and four independent Cl atoms were refined anisotropically. All other non-H atoms were given individual isotropic temperature factors providing a total of 163 refinable parameters. The weighting scheme applied was $w = 1/[\sigma^2(F_o) + 0{\cdot}0009F_o^2]$ and the final R factor was $R = 0{\cdot}064$, $R' = 0{\cdot}083$ for the 2783 observed data. A final difference map showed five peaks each of about 1 e Å^{-3} which occurred near the disordered MeOH solvent molecule, near the rotationally disordered bridging chlorines of dimer *B*, and near the disordered phenyl group of the tetraphenylborate. The three residual peaks associated with this phenyl group are consistent with a possible vibrational disorder in the plane of the ring. Final positions and thermal parameters are given in Table 1, bond lengths and angles in Table 2.* A drawing of one of the dimeric molecules is shown in Fig. 1(*a*), and a packing diagram for the whole cell is shown in Fig. 2.

Table 1. *Fractional coordinates with e.s.d.'s in parentheses and isotropic thermal parameters*

$U_{eq} = \frac{1}{3}$ trace $\tilde{U}$.

	x	y	z	U_{eq}/U_{iso} (Å^2)
Dimer *A*				
Ru(1)	0·05840 (4)	0·00000	−0·00650 (7)	0·0339
Cl(3)	0·50000	0·3192 (7)	0·50000	0·1324
Cl(4)	0·52661 (19)	0·5901 (8)	0·5972 (4)	0·1129
C(7)	0·6666 (7)	0·5893 (19)	0·6667 (7)	0·062 (5)
C(8)	0·5631 (6)	0·4211 (17)	0·3064 (7)	0·059 (5)
C(9)	0·5337 (9)	0·2829 (19)	0·2904 (15)	0·096 (7)
C(10)	0·6042 (10)	0·432 (3)	0·2645 (17)	0·129 (10)
C(1)	0·6354 (4)	0·4014 (7)	0·5520 (4)	0·043 (4)
C(2)	0·6112 (4)	0·3616 (7)	0·4664 (4)	0·039 (4)
C(3)	0·5930 (4)	0·4605 (7)	0·4021 (4)	0·037 (3)
C(4)	0·5990 (4)	0·5992 (7)	0·4234 (4)	0·036 (3)
C(5)	0·6232 (4)	0·6391 (7)	0·5090 (4)	0·037 (4)
C(6)	0·6414 (4)	0·5401 (7)	0·5733 (4)	0·034 (3)
Dimer *B*				
Ru(2)	0·06102 (5)	0·44759 (17)	0·50422 (9)	0·055
Cl(1)	0·02103 (18)	0·5395 (7)	0·5987 (3)	0·091
Cl(2)	0·00000	0·2614 (8)	0·50000	0·098
C(17)	0·1542 (9)	0·519 (3)	0·6901 (9)	0·097 (7)
C(18)	0·0855 (9)	0·3289 (23)	0·3372 (11)	0·108 (8)
C(19)	0·0383 (10)	0·228 (3)	0·3065 (18)	0·129 (10)
C(20)	0·0695 (12)	0·444 (3)	0·2706 (18)	0·144 (12)
C(11)	0·1339 (5)	0·3430 (10)	0·5731 (6)	0·065 (5)
C(12)	0·1406 (5)	0·4811 (10)	0·5958 (6)	0·066 (5)
C(13)	0·1290 (5)	0·5814 (10)	0·5325 (6)	0·053 (4)
C(14)	0·1107 (5)	0·5435 (10)	0·4464 (6)	0·071 (6)
C(15)	0·1040 (5)	0·4054 (10)	0·4237 (6)	0·083 (6)
C(16)	0·1156 (5)	0·3051 (10)	0·4870 (6)	0·074 (6)
Tetraphenylborate				
B(1)	0·2589 (6)	0·0085 (21)	0·4857 (9)	0·039 (4)
C(21)	0·2149 (3)	−0·0709 (11)	0·4030 (6)	0·040 (4)
C(22)	0·1616 (3)	−0·0380 (11)	0·3812 (6)	0·058 (5)
C(23)	0·1223 (3)	−0·1079 (11)	0·3149 (6)	0·072 (5)
C(24)	0·1363 (3)	−0·2106 (11)	0·2703 (6)	0·068 (5)
C(25)	0·1896 (3)	−0·2434 (11)	0·2920 (6)	0·075 (6)
C(26)	0·2289 (3)	−0·1736 (11)	0·3584 (6)	0·055 (4)
C(27)	0·3219 (3)	−0·0023 (14)	0·4946 (6)	0·041 (3)
C(28)	0·3332 (3)	0·0129 (14)	0·4214 (6)	0·069 (5)
C(29)	0·3858 (3)	0·0123 (14)	0·4283 (6)	0·100 (7)
C(30)	0·4270 (3)	−0·0034 (14)	0·5083 (6)	0·101 (7)
C(31)	0·4157 (3)	−0·0186 (14)	0·5814 (6)	0·097 (7)
C(32)	0·3631 (3)	−0·0181 (14)	0·5746 (6)	0·065 (5)
C(33)	0·2508 (4)	0·1836 (8)	0·4790 (6)	0·042 (4)
C(34)	0·2301 (4)	0·2443 (8)	0·3981 (6)	0·048 (4)
C(35)	0·2258 (4)	0·3865 (8)	0·3906 (6)	0·060 (5)
C(36)	0·2421 (4)	0·4679 (8)	0·4640 (6)	0·073 (5)
C(37)	0·2628 (4)	0·4072 (8)	0·5449 (6)	0·059 (5)
C(38)	0·2671 (4)	0·2651 (8)	0·5524 (6)	0·047 (4)
C(39)	0·2491 (4)	−0·0572 (11)	0·5686 (6)	0·048 (4)
C(40)	0·2173 (4)	0·0081 (11)	0·6047 (6)	0·047 (3)
C(41)	0·2075 (4)	−0·0543 (11)	0·6714 (6)	0·070 (5)
C(42)	0·2296 (4)	−0·1821 (11)	0·7019 (6)	0·073 (5)
C(43)	0·2614 (4)	−0·2474 (11)	0·6658 (6)	0·085 (6)
C(44)	0·2711 (4)	−0·1849 (11)	0·5991 (6)	0·053 (4)
Methanol solvate				
C(45)	0·5656 (8)	0·429 (3)	0·0328 (12)	0·099 (6)
C(46)	0·5301 (8)	0·414 (3)	−0·0492 (11)	0·099 (7)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Dimer *B*		Dimer *A*	
Ru(2)–Ru(2')	3·282 (3)	Ru(1)–Ru(1')	3·283 (3)
Ru(2)–Cl(1)	2·431 (7)	Ru(1)–Cl(3)	2·411 (5)
Ru(2)–Cl(2)	2·449 (6)	Ru(1)–Cl(4)	2·406 (7)
Ru(2)–C(11)	2·139 (11)	Ru(1)–C(1)	2·174 (8)
Ru(2)–C(12)	2·153 (11)	Ru(1)–C(2)	2·152 (9)
Ru(2)–C(13)	2·168 (12)	Ru(1)–C(3)	2·137 (10)
Ru(2)–C(14)	2·169 (14)	Ru(1)–C(4)	2·144 (10)
Ru(2)–C(15)	2·155 (14)	Ru(1)–C(5)	2·166 (9)
Ru(2)–C(16)	2·141 (13)	Ru(1)–C(6)	2·180 (8)
Tetraphenylborate			
B(1)–C(21)	1·644 (17)		
B(1)–C(27)	1·673 (19)		
B(1)–C(33)	1·722 (22)		
B(1)–C(39)	1·656 (21)		

Dimer *B*		Dimer *A*	
Ru(2)–Cl(1)–Ru(2')	85·21 (20)	Ru(1)–Cl(3)–Ru(1')	85·84 (13)
Ru(2)–Cl(2)–Ru(2')	84·13 (15)	Ru(1)–Cl(4)–Ru(1')	86·15 (22)
Cl(1)–Ru(2)–Cl(1')	79·01 (20)	Cl(3)–Ru(1)–Cl(4)	78·60 (18)
Cl(1)–Ru(2)–Cl(2)	79·57 (18)	Cl(3)–Ru(1)–Cl(4')	78·68 (18)
Cl(1')–Ru(2)–Cl(2)	79·84 (18)	Cl(4)–Ru(1)–Cl(4')	78·42 (22)

Discussion. There are no significant differences in bond lengths and angles between the two dimers. The apparent shortening of the Ru–Cl bonds in dimer *A* is likely to result from the high anisotropic thermal parameters of the bridging Cl atoms (see Fig. 1*b*). The

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38010 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

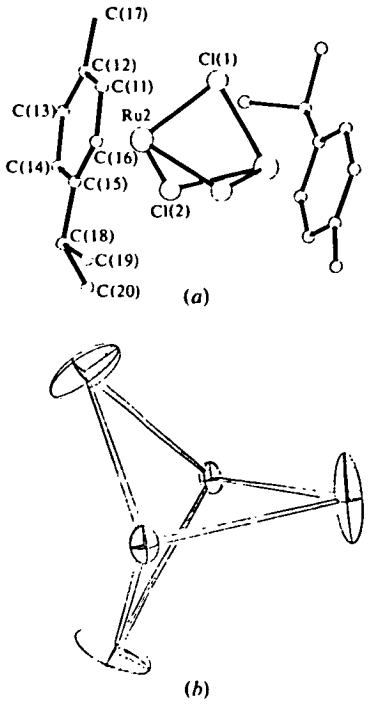

Fig. 1. (*a*) A labelled drawing of dimer *B*. The crystallographic twofold axis at $Oy\frac{1}{4}$ goes through Cl(2) and bisects the Ru(2)–Ru*(2) vector. (*b*) The triple-bridged Ru(1)Cl_3Ru*(1) group of dimer *A*. The large anisotropic components of Cl(3) and Cl(4) indicate rotational disorder about the Ru–Ru axis.

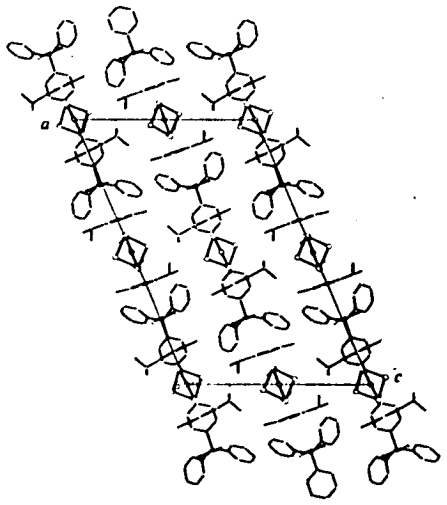

Fig. 2. Unit-cell contents viewed along **b**.

Ru···Ru distance of 3·283 Å is in the middle of the expected Ru···Ru dimer range of 3·44 to 3·08 Å (Laing & Pope, 1976; Crozat & Watkins, 1972). Both Ru atoms are in oxidation state (II) which precludes any metal–metal bonding. The Ru–Cl bond lengths lie between 2·41 and 2·45 Å with Ru–Cl–Ru′ angles in the range 84 to 86° and Cl–Ru–Cl angles of 79(±1)°. These values are in close agreement with the values found in other trichloro-bridged dimers.

The ring centroids of the η-bonded *p*-cymene groups are 1·647 and 1·642 Å from the Ru atoms of dimers *A* and *B* respectively. This compares with values of 1·622 Å in the tetranuclear complex $\{Ru(\eta\text{-}C_6H_6)OH\}_4^{4+}$ (Gould, Jones, Robertson, Tocher & Stephenson, 1982) and 1·637 Å in di-μ-chloro-bis-[chloro(η-*p*-cymene)Os^{II}] (Watkins & Fronczek, 1982). All C–C single bonds refined to within 0·01 Å of their idealized value of 1·54 Å. In neither dimer *A* nor dimer *B* are the isopropyl groups symmetrical with respect to the benzene ring. Dimer *A* has a torsion angle C(2)–C(3)–C(8)–C(9) = 26° which is identical to the conformation of the *p*-cymene in the osmium complex (Watkins & Fronczek, 1982). Dimer *B*, however, shows the corresponding torsion angle C(16)–C(15)–C(18)–C(19) = 57°.

The disordered methanol solvent molecule does not show any close intermolecular contacts.

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SYNTHESIS OF BINUCLEAR HYDROXO- AND ALKOXO-BRIDGED ARENE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

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Summary

Reactions of aqueous solutions of $[\{M(\eta\text{-}C_6H_6)Cl_2\}_2]$ (M = Ru, Os) with an excess of either NaOH or Na_2CO_3 followed by addition of $NaBPh_4$ gave as the major product $[\eta\text{-}C_6H_6(OH)M(OH)_2M(H_2O)(\eta\text{-}C_6H_6)]BPh_4$ together with some $[(\eta\text{-}C_6H_6)M(OH)_3M(\eta\text{-}C_6H_6)]BPh_4$. Recrystallisation from acetone then gave pure samples of $[M_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$. Reaction of other $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with NaOH or Na_2CO_3 gave only the $[Ru_2(\eta\text{-arene})_2(OH)_3]^+$ cations (arene = p-$MeC_6H_4CHMe_2$, $C_6H_3Me_3$, C_6Me_6). Similarly, treatment of $[\{M(\eta\text{-arene})Cl_2\}_2]$ with NaOR/ROH and $NaBPh_4$ gave the triple alkoxo-bridged complexes $[M_2(\eta\text{-arene})_2(OR)_3]BPh_4$ (M = Ru, R = Me, Et, Ph; arene = C_6H_6; M = Ru, R = Me, arene = $C_6H_3Me_3$, C_6Me_6; M = Os, R = Me; arene = C_6H_6). These compounds can also be synthesised by reaction of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4 \cdot Me_2CO$ with ROH (R = Me, Et).

As an extension of our studies on the synthesis of compounds containing —RuX_3Ru— bridging units (X = Cl^-, Br^-, I^-) [1] we present in this paper the full results [2] of our attempts to prepare and characterise binuclear η-arene-ruthenium(II) complexes containing hydroxo and alkoxo bridging ligands.

Results and discussion

a) Synthesis of binuclear hydroxo-bridged complexes

Maitlis and Kang [3] have previously shown that reaction of $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ with aqueous sodium hydroxide gave the triple hydroxo-bridged complex $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]Cl \cdot 4\,H_2O$ which was also isolated as its tetraphenylborate salt by addition of a methanolic solution of $NaBPh_4$ to a methanolic solution of the chloride salt. The reactions of the isoelectronic $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (I) compound with aqueous NaOH has also been investigated by Zelonka and Baird [4], but was reported to give unstable compounds whose formation

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and decomposition could only be followed by ^{1}H NMR spectroscopy. Thus, "addition of NaOH to D_2O solutions of I gave new species with ^{1}H NMR signals at δ 5.43 and 5.58 ppm which readily decomposed as suggested by the appearance of the resonance of free benzene".

However, we have found that reaction of an aqueous solution of I with an excess of NaOH gave, on warming, a yellow solution from which a yellow solid (II) could be precipitated by addition of $NaBPh_4$. The mull IR spectrum of II contained two ν(OH) stretching vibrations at 3615 and 3520 cm^{-1} with a shoulder at 3530 cm^{-1} (cf. $[\{Pd(OH)(PPh_3)_2\}_2](BF_4)_2$, ν(OH) 3590 cm^{-1} [5]; $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]BPh_4$, ν(OH) 3600 cm^{-1} [3]). On recrystallisation from acetone, the IR spectrum of the product showed only one ν(OH) band at 3530 cm^{-1} and good evidence for acetone of solvation (ν(CO) 1695 cm^{-1}). The ^{1}H NMR spectrum at 298 K of the initial solid II in either $(CD_3)_2CO$ or CD_3NO_2 contained a strong resonance at δ 5.33 ppm and a weak one at δ 5.56 ppm (relative intensity ca. 6 : 1) attributable to η-C_6H_6 ligands (cf Zelonka and Baird's observation [4]). In addition to BPh_4^- resonances (δ 6.9—7.70 ppm) there was a broad weak resonance at δ 2.60 ppm which probably arises from the hydroxo protons *. In support of this conclusion, loss of this latter signal occurred on standing, probably because of facile H/D exchange with the solvent (cf. similar observations for $[\{M(OH)(PR_3)_2\}_2](BF_4)_2$ (M = Pd, Pt) [5] and $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]BPh_4$ [3]). The ^{13}C-{^{1}H} NMR spectrum of II in CD_3NO_2 also showed two η-C_6H_6 resonances at δ 77.8 (strong) and 79.4 (weak) ppm. The product recrystallised from acetone showed one η-C_6H_6 resonance at δ 5.56 ppm when its ^{1}H NMR spectrum was run in CD_3NO_2 at 298 K, and one ^{13}C-{^{1}H} NMR resonance at δ 79.4 ppm.

The same solid II was precipitated if an aqueous solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ was treated with an excess of Na_2CO_3 and then $NaBPh_4$ added to the solution. By using D_2O rather than H_2O, this method afforded a good synthetic route to the corresponding deuteroxo product. This deuterated material provided further evidence for the assignment of the IR bands in II at ca 3600 cm^{-1} to ν(OH) vibrations since these were absent in the former, being replaced by bands at 2595 and 2670 cm^{-1} which could be attributed to ν(OD) stretching vibrations (cf. $[\{Pt(OD)(PPh_3)_2\}_2](BF_4)_2$ (ν(OD) 2650 cm^{-1}) [5], $[Rh_2(\eta\text{-}C_5Me_5)_2(OD)_3]BPh_4$ (ν(OD) 2450 cm^{-1}) [3]).

Furthermore, on leaving II in $(CD_3)_2CO$, precipitation of some yellow solid slowly occurred and the IR spectrum of this solid showed bands at 2600 cm^{-1} (ν(OD)), 3530 cm^{-1} (ν(OH)) and solvent $(CD_3)_2CO$ (ν(CO) 1695 cm^{-1}). The ^{1}H NMR spectrum of the material in CD_3NO_2 contained one strong η-C_6H_6 resonance at δ 5.56 ppm.

Thus, all this evidence clearly indicates that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of either aqueous NaOH or Na_2CO_3 gives two cationic products which can be isolated by addition of $NaBPh_4$. Furthermore the major product

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* This assignment is supported by similar assignments in related complexes e.g. $[\{Pt(OH)(PEt_3)_2\}_2](BF_4)_2$ (δ(OH) 2.85 ppm) and $[\{Pd(OH)(PPh_3)_2\}_2](BF_4)_2$ (δ(OH) 2.00 ppm) [5]. However, earlier studies also revealed that the chemical shift of the hydroxo protons can vary considerably from compound to compound e.g. $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]BPh_4$ (δ(OH) 4.95 ppm), $Fe_2(CO)_6P(p\text{-}C_6H_4Me_2)_2OH$ (δ(OH) −2.86 ppm) [6] and $[Ru_2(PMe_2Ph)_6(OH)_3]BPh_4$ (δ(OH) −2.10 ppm) [7].

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA FOR SOME BINUCLEAR HYDROXO- AND ALKOXO-BRIDGED RUTHENIUM (II) AND OSMIUM (II) COMPLEXES

Compound	Analyses (%) [a]		Λ_m [b]
	C	H	
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]BPh_4$ [c]	56.5 (57.9)	4.9 (5.0)	61.0
$[C_6H_6Ru(OH)_3RuC_6H_6]BPh_4 \cdot Me_2CO$	59.7 (59.5)	5.2 (5.2)	55.0
$[C_6H_6(OD)Ru(OD)_2Ru(D_2O)C_6H_6]BPh_4$	58.6 (57.5)	3.9 (4.2)	
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]Cl \cdot 2H_2O$ [c]	28.6 (28.8)	4.4 (4.2)	168.0 [d]
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]Br \cdot 3H_2O$ [c]	26.0 (25.7)	4.7 (4.1)	
$[C_6H_6(OH)Os(OH)_2Os(H_2O)C_6H_6]BPh_4$ [c]	47.9 (46.9)	3.9 (4.0)	83.0
$[(C_6H_3Me_3)Ru(OH)_3Ru(C_6H_3Me_3)]BPh_4$	61.2 (62.0)	5.8 (5.8)	55.0
$[(C_6H_3Me_3)Ru(OH)_3Ru(C_6H_3Me_3)]Cl \cdot 3H_2O$	37.2 (37.1)	5.3 (5.2)	100.0 [d]
$[(MeC_6H_4CHMe_2)Ru(OH)_3Ru(MeC_6H_4CHMe_2)]BPh_4$	63.1 (62.9)	6.3 (6.1)	70.0
$[C_6Me_6Ru(OH)_3RuC_6Me_6]Cl \cdot 4H_2O$	41.1 (42.1)	6.5 (6.9)	50.0 [e]
$[C_6H_6Ru(OMe)_3RuC_6H_6]BPh_4$	60.5 (60.8)	5.3 (5.3)	68.0
$[C_6H_6Ru(OMe)_3RuC_6H_6]PF_6$	30.3 (30.2)	3.6 (3.5)	54.0
$[C_6H_6Ru(OEt)_3RuC_6H_6]BPh_4$	61.9 (62.1)	5.8 (5.8)	50.0
$[C_6H_6Ru(OEt)_3RuC_6H_6]PF_6$	33.7 (33.9)	4.2 (4.2)	
$[C_6H_6Ru(OPh)_3RuC_6H_6]BPh_4$	67.6 (67.8)	5.2 (5.0)	52.0 [e]
$[C_6H_6Os(OMe)_3OsC_6H_6]BPh_4$	48.1 (49.3)	4.8 (4.3)	54.0 [e]
$[C_6Me_6Ru(OMe)_3RuC_6Me_6]BPh_4$	65.4 (65.2)	7.3 (7.0)	54.0
$[C_6H_3Me_3Ru(OMe)_3RuC_6H_3Me_3]BPh_4$	63.3 (63.2)	6.2 (6.3)	55.0

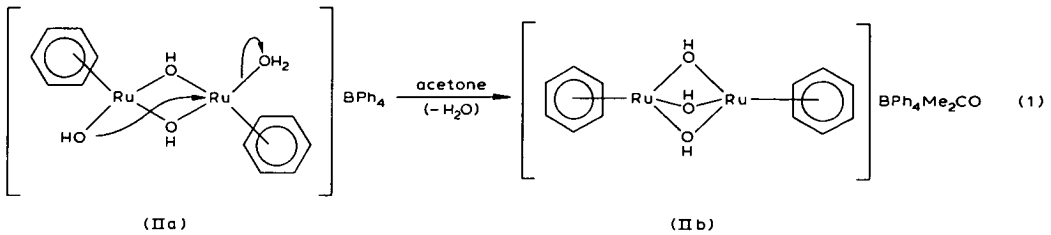
[a] Calculated figures in parenthesis. [b] Molar conductivities (S cm^2 mol^{-1}) measured in CH_3NO_2 (unless stated) at 10^{-3} mol dm^{-3} concentration. [c] IR and ^1H NMR evidence indicate these samples contain small amounts of the appropriate triple hydroxo bridged complex $[(arene)M(OH)_3M(arene)]BPh_4$. [d] Measured in water. [e] Not very soluble, measured at 5×10^{-4} mol dm^{-3} concentration.

IIa [characterised by two ν(OH) vibrations at 3615, 3520 cm^{-1} and one η-C_6H_6 resonance at δ 5.33 ppm (^1H), δ 77.8 ppm (^{13}C)] is converted irreversibly and completely, by recrystallisation from acetone, into the minor product IIb [characterised by one ν(OH) vibration at 3530 cm^{-1} and one η-C_6H_6 resonance at δ 5.56 ppm (^1H) and δ 79.4 ppm (^{13}C)].

On the basis of its NMR and IR spectra, together with analytical and conductivity data (Table 1), compound IIb is formulated as the triple hydroxo-bridged complex $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$. Further support for this proposal comes from preliminary X-ray structural analysis studies [8] on the corresponding $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OH)_3]Cl\ 3\ H_2O$ (see below).

The nature of compound IIa is less clear-cut. Both analytical data (Table 1) and integration of the ^1H NMR spectrum (in which IIa is the major species) suggested two benzene rings per BPh_4^- and conductivity measurements in CH_3NO_2 over a concentration range gave a linear $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plots of slope 214 which is characteristic of that expected for a 1 : 1 electrolyte [9]. Therefore, in the absence of any X-ray structural data, we tentatively suggest that IIa should be formulated as the di-hydroxo-bridged cation $[(\eta\text{-}C_6H_6)(OH)Ru(OH)_2Ru(H_2O)(\eta\text{-}C_6H_6)]BPh_4$. This structure is consistent with both the observed IR spectrum (more than one ν(OH)) and the facile irreversible rearrangement of IIa to IIb (eq. 1) on recrystallisation from acetone.

Similar double-bridged binuclear intermediates have been proposed elsewhere in reactions leading to complexes such as $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]PF_6$ [10], $[Ru_2(OH)_3(PR_3)_6]BPh_4$ [7] and $[Ru_2Cl_3(PR_3)_6]Cl$ [11]. The observation of



only one η-C_6H_6 resonance for IIa can be rationalised on the basis of either fast intramolecular rearrangement processes involving terminal and bridging hydroxo (or aqua) groups and/or facile proton transfer between coordinated hydroxo and aqua groups.

Similarly, reaction of $[\{Os(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of aqueous NaOH followed by addition of $NaBPh_4$ gave a product whose IR spectrum contained two ν(OH) bands at 3580, 3530 cm^{-1} and whose ^1H NMR spectrum in CD_3NO_2 showed a strong η-C_6H_6 resonance at δ 5.97 ppm. This was formulated as $[(\eta\text{-}C_6H_6)(OH)Os(OH)_2Os(H_2O)(\eta\text{-}C_6H_6)]BPh_4$. A small amount of $[Os_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4$ [ν(OH), 3495 cm^{-1}; ^1H NMR in CD_3NO_2: δ 6.08 ppm (η-C_6H_6)] was also present.

In contrast, reaction of $[\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2]$ with an aqueous solution of NaOH, followed by addition of $NaBPh_4$ yielded a yellow solid shown by elemental analysis and conductance measurements (Table 1), IR spectrum (ν(OH) 3600 cm^{-1}) and ^1H NMR spectrum in CD_3NO_2 (Table 2) to contain only the triple hydroxo-bridged complex $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OH)_3]BPh_4$. As for the corresponding η-C_6H_6 complexes, facile H/D exchange of the hydroxo protons occurred in deuterated solvents, although unlike the $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]^+$ cation [3] no exchange of the methyl protons was observed.

If the solvent was removed under vacuo from the $[\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2]$/NaOH reaction mixture before addition of $NaBPh_4$, a crystalline yellow solid which analysed for $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3\,H_2O$ was deposited *. Although strong broad water bands centred at ca. 3300 cm^{-1} obscured any ν(OH) bands in the IR spectrum of this compound, a preliminary X-ray structural analysis [8] has confirmed the presence of the —$Ru(OH)_3Ru$— bridging unit.

Likewise, reaction of $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ with an excess of NaOH in water gave a product formulated as $[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Cl \cdot 4\,H_2O$ (one η-C_6Me_6 resonance in its ^1H NMR spectrum at δ 2.05 ppm) ** and $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4\text{-}CHMe_2)Cl_2\}_2]$ on treatment with an excess of NaOH or Na_2CO_3 in water followed by addition of $NaBPh_4$ gave a pure sample of $[Ru_2(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)_2\text{-}(OH)_3]BPh_4$ (ν(OH) 3550 cm^{-1}) (see Table 1 and 2 and $^{13}C\text{-}\{^1H\}$ NMR spectrum in Experimental section). Thus it appears that the greater the degree of

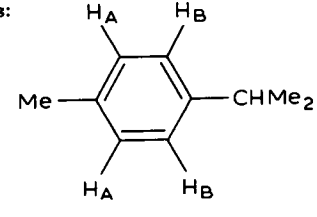
* A solid can also be isolated from the $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$/NaOH(aq) reaction mixture by slow evaporation of the solvent. Initially this was claimed to be $[Ru_2(\eta\text{-}C_6H_6)_3(OH)_3]Cl \cdot 3\,H_2O$ [2]. However, if this material is redissolved in water and treated with $NaBPh_4$, the product precipitated has the same IR and ^1H NMR spectra as that found for product II, i.e. it is a mixture of the cations $[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]^+$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]^+$.

** $[Ru_2(\eta\text{-}C_6Me_6)_2(OH)_3]Y$ (Y = Cl^-, PF_6^-) has been recently reported to be an active homogeneous catalyst for the disproportionation of acetaldehyde to acetic acid and ethanol but its method of synthesis has not been published [12].

TABLE 2 HYDROGEN-1 NMR DATA FOR SOME BINUCLEAR HYDROXO AND ALKOXO COMPLEXES AT 298 K

Compound	Solvent	δ ppm [a,b]	
		η-arene	OH^-/OR^-
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]BPh_4$ [c]	CD_3NO_2	5.33 (s)	2.60 (s)
$[C_6H_6Ru(OH)_3RuC_6H_6]BPh_4 \cdot Me_2CO$	CD_3NO_2	5.56 (s)	2.60 (s)
$[C_6H_6(OD)Ru(OD)_2Ru(D_2O)C_6H_6]BPh_4$ [c]	$(CD_3)_2CO$	5.33 (s)	
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6)]Cl \cdot 2H_2O$ [c,d]	D_2O	5.88 (s)	*e*
$[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]Br \cdot 3H_2O$ [c,d]	D_2O	5.85 (s)	*e*
$[C_6H_6(OH)Os(OH)_2Os(H_2O)C_6H_6]BPh_4$ [c]	$(CD_3)_2CO$	5.93 (s)	*e*
	CD_3NO_2	5.97 (s)	*e*
$[C_6H_3Me_3Ru(OH)_3RuC_6H_3Me_3]BPh_4$	$(CD_3)_2CO$	4.69 (s) (H); 2.04 (s) Me	2.32 (s)
$[C_6H_3Me_3Ru(OH)_3RuC_6H_3Me_3]Cl \cdot 3H_2O$ [d]	D_2O	5.32 (s) H; 2.55 (s) Me	*e*
$[(MeC_6H_4CHMe_2)Ru(OH)_3Ru(MeC_6H_4CHMe_2)]BPh_4$ [f]	$CDCl_3$	4.76 (ΔH_AH_B 30 Hz, *J* 6.0 Hz) 2.49 (sp $CHMe_2$) 1.90 (s, CH_3) 1.18 (d, CH_3 of $CHMe_2$, *J* 7.0 Hz)	1.65 (s)
$[(C_6Me_6)Ru(OH)_3Ru(C_6Me_6)]Cl \cdot 4H_2O$	CD_3NO_2	2.05 (s)	*e*
$[C_6H_6Ru(OMe)_3Ru(C_6H_6)]BPh_4$	$(CD_3)_2CO$	5.48 (s)	4.42 (s)
$[C_6H_6Ru(OMe)_3RuC_6H_6]PF_6$	$(CD_3)_2CO$	5.66 (s)	4.68 (s)
$[C_6H_6Ru(OEt)_3RuC_6H_6]BPh_4$	$(CD_3)_2SO$	5.43 (s)	4.50 (q) 1.35 (t) ($^3J(CH_2CH_3)$ 7.0 Hz)
$[C_6H_6Ru(OEt)_3RuC_6H_6]PF_6$	$(CD_3)_2CO$	5.50 (s)	4.33 (q) 1.58 (t) ($^3J(CH_2CH_3)$ 7.0 Hz)
$[C_6H_6Ru(OPh)_3RuC_6H_6]BPh_4$	CD_3NO_2	5.12 (s)	6.95 (m) [g]
$[C_6H_6Os(OMe)_3OsC_6H_6]BPh_4$	$(CD_3)_2CO$	6.15 (s)	4.63 (s)
$[C_6Me_6Ru(OMe)_3RuC_6Me_6]BPh_4$	$CDCl_3$	1.97 (s)	4.00 (s)
$[(C_6H_3Me_3)Ru(OH)_3Ru(C_6H_3Me_3)]BPh_4$	$(CD_3)_2CO$	5.08 (s) (H); 2.16 (s) (Me)	4.36 (s)

[a] Reference standard-internal Me_4Si lock unless otherwise stated. [b] Where appropriate BPh_4^- multiplets observed between δ6.90—7.60 ppm. [c] These samples contain small amounts of appropriate triple hydroxo-bridged cation [arene $Ru(OH)_3Ru$ arene]Y (Y = BPh_4^-, Cl^- or Br^-) whose NMR parameters are not given (see Experimental section for values). [d] Reference standard-external Me_4Si capillary. [N.B. As discussed earlier [10], the high frequency shift of the η-arene resonances here compared to those in the corresponding BPh_4^- salts is attributed mainly to the change of reference from internal Me_4Si lock to external Me_4Si capillary. [e] Not observed. [f] Labelling of *p*-cymene protons:



Chemical shift difference calculated from line positions using formula $\Delta(H_AH_B) = [(\upsilon_1 - \upsilon_4)(\upsilon_2 - \upsilon_3)]^{1/2}$ since an AB rather than AA′BB′ pattern was observed. Midpoint of AB resonance is quoted. [g] Partially masked by BPh_4^- resonances. s (singlet); d (doublet); t (triplet); q (quartet); sp (septet); m (multiplet).

substitution of the arene ring, the greater the tendency to form the triple hydroxo-bridged complex, although it is likely that kinetically labile double hydroxo bridged complexes analogous to IIb are involved in the reaction.

Finally, attempts to isolate the cations IIa and IIb as their hexafluorophosphate salts by addition of NH_4PF_6 to the yellow solution obtained by reacting $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with aqueous NaOH, yielded an unexpected product. No precipitate was found immediately on addition of NH_4PF_6, but on standing for several days, a yellow crystalline solid was deposited whose IR spectrum showed a series of sharp intense bands at 3095, 3210, 3300, and 3365 cm^{-1}. These were assigned to ν(NH) stretching frequencies, whilst the broad absorptions at 1660 cm^{-1} (with shoulders at 1670 and 1630 cm^{-1}) and 452 cm^{-1} could be attributed to δ(NH) deformations and ν(Ru—N) stretches, respectively (cf. the vibrational modes associated with Ru—NH_3 for the cation $[Ru(\eta\text{-}C_6H_6)(NH_3)_2Cl]^+$ [13]. Also, no bands attributable to ν(RuCl) stretching modes were observed in the IR spectrum. The ^1H NMR spectrum of this solid in $(CD_3)_2CO$ contained one η-C_6H_6 signal at δ 5.99 ppm plus a broad hump centred at δ 3.79 ppm (NH_3 protons). The intensity ratio from the ^1H NMR spectrum indicated three ammonia groups per coordinated benzene ring which, together with elemental analysis figures suggested the formulation $[Ru(\eta\text{-}C_6H_6)(NH_3)_3](PF_6)_2$. The molar conductivity of this complex in CH_3NO_2 was 178 S cm^2 mol^{-1} (for a 10^{-3} mol dm^{-3} solution) and a plot of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ gave a slope of 437, both consistent with that expected for a 1 : 2 electrolyte (cf $[Ni(phen)_3]Cl_2$, Λ_m = 118 S cm^2 mol^{-1}; slope = 420 [14]).

Presumably this trisammine complex is formed from the reaction of the cations IIa and/or IIb with ammonium ion which can act as a weak acid protonating the OH^- bridges to form the trisaqua intermediate $[Ru(\eta\text{-}C_6H_6)(H_2O)_3]^{2+}$ which might then undergo substitution of water by ammonia groups. (cf. the related reactions of $[Ru_2(OH)_3(PMe_2Ph)_6]^+$ with acids in various solvents (S) which gave $[Ru(S)_3(PMe_2Ph)_3]^{2+}$ species [7]). Alternatively since excess NaOH is present, H^+ may be removed by OH^-, but this would have to be followed by bridge cleavage and replacement of OH^- groups by NH_3, which seems unlikely in view of the apparent stability of these hydroxo bridges towards Lewis bases (see below).

b) Synthesis of binuclear alkoxo-bridged complexes

Earlier, we showed that the $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ cation underwent facile bridge cleavage reactions with a variety of Lewis bases to give monomeric compounds of type $[Ru(\eta\text{-}C_6H_6)ClL_2]PF_6$, $[Ru(\eta\text{-}C_6H_6)Cl_2L]$ and/or $[RuCl_2L_4]$ (L = C_5H_5N, Et_2S, Me_2SO, PR_3 etc). In contrast, product II ($[C_6H_6(OH)Ru(OH)_2Ru(H_2O)C_6H_6]BPh_4$ and $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4$) does not react with an excess of tertiary phosphines (PR_3 = PPh_3, PMe_2Ph, PEt_2Ph) in acetone, even under reflux conditions for prolonged periods, (cf. $[\{Pt(OH)(PR_3)_2\}_2](BF_4)_2$ does not react with more PR_3 [5]), the only product isolated being $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$ (IIb).

However, refluxing $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$ (IIb) in methanol produced a yellow solution which deposited a yellow crystalline solid on cooling. The IR spectrum of this solid showed no bands at ca. 3600 cm^{-1} but the presence of a strong broad band at 1050 cm^{-1} indicated the presence of methoxide

groups (cf. $Ti(OMe)_4$ with ν(O—C) 1032 cm^{-1} [15]). Since the ^1H NMR spectrum in $(CD_3)_2CO$ consisted of BPh_4^- multiplets centred at ca. δ 6.90 and 7.30 ppm, a η-C_6H_6 peak at δ 5.48 ppm and a singlet at δ 4.42 ppm (assigned to —OMe protons) in the intensity ratio 20 : 12 : 9 respectively, this compound was formulated as the triple methoxo-bridged complex $[Ru_2(C_6H_6)_2(OMe_3)]BPh_4$. This formulation was supported by elemental analyses and conductivity measurements in CH_3NO_2 which indicated a 1 : 1 electrolyte. The ethoxo complex $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3]BPh_4$ was also prepared by refluxing IIb in ethanol (see Tables 1 and 2 for characterisation). Like the $[Ru(\eta\text{-}C_6H_6)(NH_3)_3]^{2+}$ cation discussed earlier, these alkoxo compounds are probably formed via protonation of the hydroxo bridges by the weak acid ROH to form the $[Ru(\eta\text{-}C_6H_6)(H_2O)_3]^{2+}$ cation, which can then react rapidly with OR^- to give monomeric alkoxo species such as $[Ru(\eta\text{-}C_6H_6)OR(H_2O)_2]^+$ and $[Ru(\eta\text{-}C_6H_6)(OR)_2H_2O]$. As discussed elsewhere for the analogous $[Ru_2(\eta\text{-}C_6H_6)_2Cl_3]^+$ [10] and $[Ru_2Cl_3(PR_3)_6]^+$ [11] cations, facile intermolecular coupling reactions of these solvated monomers would then give the $[Ru_2(\eta\text{-}C_6H_6)_2(OR)_3]^+$ cations.

These alkoxo cations have also been prepared by reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with freshly prepared NaOR (R = Me, Et) in alcoholic solvents followed by addition of $NaBPh_4$. Unlike the binuclear hydroxo-bridged cations, their PF_6^- salts were readily isolated by addition of NH_4PF_6 to the above reaction mixture. Likewise reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with NaOPh in methanol and then addition of $NaBPh_4$ gave the triple phenoxo-bridged cation $[Ru_2(\eta\text{-}C_6H_6)_2)OPh)_3]BPh_4$. In fact, the following compounds have been successfully synthesised by reaction of $[\{M(arene)Cl_2\}_2]$ with NaOMe; $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OMe)_3]BPh_4$; $[Os_2(\eta\text{-}C_6H_6)_2(OMe)_3]BPh_4$ and $[Ru_2(\eta\text{-}C_6Me_6)_2(OMe)_3]BPh_4$ (see Experimental section and Tables 1 and 2 for details).

However, attempts to synthesise longer chain alkoxides such as i-PrO or n-BuO using either the $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO/ROH$ or $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$/NaOR routes were unsuccessful since extensive decomposition occurred and no ruthenium complexes could be isolated from the reaction mixture. This decomposition is believed to occur via ruthenium hydride formation, generated by facile β-elimination steps from intermediate alkoxo species. Good evidence for hydride formation comes from a recent communication on the isolation of the complexes $[Ru_2(\eta\text{-arene})_2X(H)_2]PF_6$ (X = Cl^-, arene = C_6Me_6; $C_6H_3Me_3$; X = H^-, arene = $C_6H_3Me_3$), obtained by reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ with aqueous solutions containing isopropoxide ions [16]. Similar hydride complexes are probably formed in reactions between the benzene complexes and longer chain alkoxides, but due to the comparative weakness of the ruthenium—benzene bonds, loss of benzene and subsequent product decomposition results.

Finally, preliminary studies indicate that the binuclear hydroxo- and alkoxo-bridged complexes described in this paper react with a wide range of weak acids and other reagents [17] and these studies will be described in a future publication.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000—250 cm^{-1} on Perkin Elmer 447 and 557 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and carbon-13 NMR spectra on a Varian CFT 20 spectrometer operating at 20 MHz (^{13}C chemical shifts are quoted in ppm to high frequency of TMS). Melting points were determined with a Köfler hot stage microscope and are uncorrected. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Conductivity vs. concentration data were obtained over a range of concentrations (2×10^{-3} to 5×10^{-3} dm^{-3} mol) for several of the compounds and a plot of Λ_e (equivalent conductance) vs. $C_e^{1/2}$ (concentration in equivalents dm^{-3}) gave a straight line which on extrapolation to $C_e^{1/2} = 0$ gave Λ_0. A subsequent plot of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ gave a straight line whose slope is a function of the ionic charges [9]. Thus, the slopes obtained for various samples were compared with those for known 1 : 1 and 2 : 1 electrolytes and hence the electrolyte type could be determined.

Materials

Ruthenium trichloride trihydrate and sodium hexachloroosmate(IV) (Johnson Matthey Ltd.), α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) (Eastman Chemicals) CD_3NO_2, cyclohexa-1,3-diene hexamethyl benzene (Aldrich Chemicals); NaOH, $NaBPh_4$ (BDH); sodium metal (Fisons); NH_4PF_6, $AgPF_6$ (Alfa). The compounds 1,3,5-trimethylcyclohexa-1,4-diene, and cyclohexa-1,4-diene were prepared by the standard Birch reduction of the corresponding arenes [18]. The compounds $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, $C_6H_3Me_3$, p-$MeC_6H_4CHMe_2$] were prepared as described elsewhere [1c] using purified "$RuCl_3\ x\ H_2O$". The compound $[\{Os(\eta\text{-}C_6H_6)Cl_2\}]_2$ was prepared in low yield (33%) from $Na_2[OsCl_6]$ and 1,3-cyclohexadiene in ethanol [1c] and $\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2$ by reaction of $[\{Ru(p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ with C_6Me_6 [19]. All reactions were carried out under an atmosphere of nitrogen. Analytical and conductivity data for some of the binuclear compounds are given in Table 1 and ^1H NMR data in Table 2.

"Di-μ-hydroxo(aqua)hydroxobis[(η-benzene)ruthenium(II)] tetraphenylborate"

Method A. Addition of an excess of $NaBPh_4$ (0.20 g; 0.60 mmol) in water (5 cm^3) to the yellow solution obtained from the reaction of $[\{Ru(\eta\text{-}C_6H_6)\text{-}Cl_2\}_2]$ (0.10 g; 0.20 mmol) and NaOH (0.15 g; 4.0 mmol) in warm water (20 cm^3) gave a yellow precipitate which was filtered off and air-dried. The filtrate deposited more of the complex if left to stand (0.09 g, 65%) m.p. 190°C (decomp) [ν(OH) 3520, 3615 cm^{-1}; δ(Ru—OH) 1135 cm^{-1}; ν(RuO) 490 cm^{-1} (mull)] [$^{13}C\text{-}\{^1H\}$ NMR in CD_3NO_2 (298 K): δ 77.8 (s) ppm, δ 121—136 ppm (BPh_4^-)] slope of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plot in CH_3NO_2 = 214.

A small amount of tri-μ-hydroxobis[(η-benzene)ruthenium(II)] tetraphenylborate was also precipitated from this solution as evidenced by infrared [ν(OH) 3530 cm^{-1} (mull)] ^1H NMR (CD_3NO_2): δ 5.56 (s) ppm (weak)] and $^{13}C\text{-}\{^1H\}$

NMR [δ 79.4 ppm; δ 121—136 ppm (BPh_4^-) data. Recrystallisation of this product from acetone gives a pure sample of tri-μ-hydroxobis[(η-benzene)-ruthenium(II)] tetraphenylborate acetone solvate (1 : 1) (m.p. 185°C (decomp)) [ν(OH) 3530 cm^{-1}; ν(CO) 1695 cm^{-1}; δ(RuOH) 1135 cm^{-1}; ν(RuO) 510 cm^{-1} (mull)], $^{13}C-\{^1H\}$ NMR in CD_3NO_2 (298 K): δ 79.4 (s) ppm. Similarly prepared was "di-μ-hydroxo(aqua)hydroxo bis[(η-benzene)osmium(II) tetraphenylborate" from $[\{Os(\eta\text{-}C_6H_6)Cl_2\}_2]$ and excess of NaOH followed by addition of $NaBPh_4$ (m.p. 195°C (decomp)) (60%) [ν(OH) 3580, 3530 cm^{-1}; δ(OsOH) 1135 cm^{-1} (mull)]. A small amount of $[Os_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4$ was also precipitated from solution [ν(OH) 3495 cm^{-1}] ^1H NMR in $(CD_3)_2CO$ at 298 K: δ 6.13 (s) ppm.

Method B. The complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.10 g: 0.20 mmol) was dissolved in warm water (5 cm^3) and filtered. The orange solution was shaken with an excess of Na_2CO_3 (0.20 g; 2.0 mmol) for 2 hours to give a yellow solution, which on addition of $NaBPh_4$ (0.20 g; 0.60 mmol) gave the complex as a yellow precipitate (0.08 g, 59%). Recrystallisation from acetone then gave $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4 \cdot Me_2CO$.

Di-μ-deuteroxo(deuterium oxide)deuteroxo bis[(η-benzene)ruthenium(II)] tetraphenylborate

As for method B above but using D_2O instead of H_2O to give a yellow solid, m.p. 200°C (decomp) [ν(OD) 2595, 2670 cm^{-1}; ν(RuO) 475 cm^{-1} (mull)]. A small amount of tri-μ-deuteroxobis[(η-benzene)ruthenium(II)] tetraphenylborate is also precipitated (ν(OD) 2600 cm^{-1}) and this can be obtained in a pure state (as an acetone solvate) by recrystallisation from $(CD_3)_2CO$.

Di-μ-hydroxo(aqua)hydroxobis[(η-benzene)ruthenium(II)] chloride hydrate (1/2)

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.10 g; 0.20 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol). The solution was warmed giving a yellow solution, filtered and left to stand under vacuo (water pump) for 2 hours to give a yellow solid (0.04 g, 42%) (m.p. 132°C (decomp)) [ν(OH) 3300(br) cm^{-1}; δ(HOH) 1620 cm^{-1}; ν(RuO) 495 cm^{-1} (mull)]. Addition of $NaBPh_4$ to a concentrated aqueous solution of this compound gave "$[Ru_2(C_6H_6)_2(OH)_3H_2O]BPh_4$" [ν(OH) 3520, 3615 cm^{-1} (mull)] and a small amount of $[Ru_2(C_6H_6)_2(OH)_3]BPh_4$ [ν(OH) 3530 cm^{-1}].

Di-μ-hydroxo(aqua)hydroxo bis[(η-benzene)ruthenium(II)]bromide hydrate (1/3)

As above from $[\{Ru(\eta\text{-}C_6H_6)Br_2\}_2]$ and excess of NaOH (m.p. 150°C (decomp)) [ν(OH) 3250(br) cm^{-1}; δ(HOH) 1650 cm^{-1}; ν(RuO) 460 cm^{-1} (mull)].

Tri-μ-hydroxobis[(η-mesitylene)ruthenium(II)] tetraphenylborate

Method A. Addition of an excess of $NaBPh_4$ (0.20 g; 0.60 mmol) in water (5 cm^3) to the yellow solution obtained from the reaction of $[\{Ru(\eta\text{-}C_6H_3Me_3)\text{-}Cl_2\}_2]$ (0.12 g; 0.20 mmol) and NaOH (0.15 g; 4.0 mmol) in warm water (20 cm^3) gave a yellow precipitate which was filtered off and air dried. (0.20 g;

67%) (m.p. 110—111°C) [ν(OH) 3600 cm^{-1} δ(RuOH) 1149 cm^{-1}, ν(RuO) 490 cm^{-1} (mull)].

Tri-μ-hydroxobis[(η-mesitylene)ruthenium(II)] chloride hydrate (1/3)

The compound [$\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2$] (0.12 g; 0.20 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol). The solution was warmed to give a yellow solution, filtered and left to stand under vacuo (water pump) for two hours to give a yellow crystalline solid, m.p. 185°C (decomp) [ν(OH) 3300 cm^{-1}; δ(HOH) 1670 cm^{-1}; ν(RuO) 489 cm^{-1} (mull)].

Tri-μ-hydroxobis[(η-p-cymene)ruthenium(II)] tetraphenylborate

Method A. The compound [$\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2$] (0.25 g; 0.40 mmol) mmol) was dissolved in water (10 cm^3) and NaOH (0.15 g; 4.0 mmol) was added. The solution was stirred and gently warmed for two hours. It was then filtered and excess $NaBPh_4$ (0.20 g; 0.60 mmol) in water (5 cm^3) was added to give a gummy precipitate. Vigorous stirring for several hours gave a yellow powdery precipitate which was filtered off and washed with water and light petroleum (b.p. 60—80°C) (0.11 g; 32%) [ν(OH) 3550 cm^{-1} (mull)] $^{13}C\text{-}\{^1H\}$ NMR $CDCl_3$ (298 K): δ 121—136 ppm (BPh_4^-), δ 96.4 (A), 93.0 (B), 77.4 (C), 74.8 (D), 31.1 (E), 22.4 (F), 17.9 (G) ppm *.

Method B. As above but using an excess of Na_2CO_3 rather than NaOH (0.26 g; 75%) slopes of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ in CH_3NO_2 = 100.

Tri-μ-hydroxobis[(η-hexamethyl)benzene)ruthenium(II)] chloride hydrate (1/4)

Method A. The compound [$\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2$] (0.10 g; 0.15 mmol) was dissolved in hot water (20 cm^3). The solution was filtered, an excess of NaOH (0.30 g; 8.0 mmol) added and the solution refluxed for two hours. On cooling a pale green solid was deposited which was filtered off, washed with water and air dried (0.08 g; 78%) (m.p. 192—195°C) [ν(OH) 3420 cm^{-1}; δ(HOH) 1660 cm^{-1}; ν(RuO) 500 cm^{-1}].

Tris(ammine)(η-benzene)ruthenium(II) hexafluorophosphate

The compound [$\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2$] (0.02 g; 0.40 mmol) was dissolved in water (10 cm^3) with NaOH (0.15 g; 4.0 mmol) and warmed. Addition of an excess of NH_4PF_6 (0.16 g; 1.0 mmol) gave a yellow crystalline precipitate after 3 days (m.p. >240°C (decomp)) (0.15 g, 36%) [ν(NH) 3095; 3210; 3300, 3365 cm^{-1}; δ(NH) 1670, 1660, 1630 cm^{-1}; ν(RuN) 452 cm^{-1} (mull)]. Found: C, 14.1; H, 2.9; N, 8.1. Calcd. for $C_6H_{15}F_{12}N_3P_2Ru$: C, 13.8; H, 2.9; N, 8.1%. Conductivity in CH_3NO_2 at 303 K: Λ_m (10^{-3} mol dm^{-3}) = 178 S cm^2 mol^{-1}; Slope of $\Lambda_0 - \Lambda_e$ vs $C_e^{1/2}$ plot = 437 ^1H NMR in $(CD_3)_2CO$ (298 K) δ 5.99 (s) (η-C_6H_6), 3.79 ppm (br) (NH_3).

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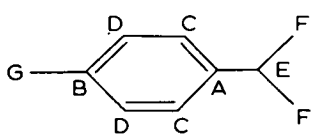
* Labelling of *p*-cymene carbons



Tri-μ-methoxobis[(η-benzene)ruthenium(II)] tetraphenylborate

Method C. The compound [{$Ru(\eta\text{-}C_6H_6)Cl_2$}$_2$] (0.10 g; 0.20 mmol) was added to a freshly prepared solution of NaOMe [Na (ca. 0.10 g) in MeOH (10 cm^3)] and the solution was gently warmed to give a yellow solution which deposited a yellow solid on addition of $NaBPh_4$ and which was washed with methanol and air-dried. (0.12 g; 81%) (m.p. 198°C (decomp)) [ν(CO) 1050 cm^{-1}; δ(Ru—O—C) 1145 cm^{-1}; ν(RuO) 550 cm^{-1} (mull)]. Similarly prepared from [{$Ru(\eta\text{-}C_6H_6)Cl_2$}$_2$] and NaOEt was tri-μ-ethoxobis[(η-benzene)ruthenium(II)] tetraphenylborate; m.p. 220°C (decomp) [ν(CO) 1050 cm^{-1}; ν(RuO) 570 cm^{-1} (mull)]. If NH_4PF_6 is used instead of $NaBPh_4$, the complexes tri-μ-methoxobis[(η-benzene)ruthenium(II)] hexafluorophosphate (m.p. 200°C (decomp)) [ν(CO) 1040 cm^{-1}; δ(RuOC) 1150 cm^{-1} (mull)] (slope of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ in CH_3NO_2 = 245) and Tri-μ-ethoxobis[(η-benzene)ruthenium(II)] hexafluorophosphate (m.p. 190°C (decomp)) [ν(CO) 1050 cm^{-1}; δ(RuOC) 1150 cm^{-1}] could be prepared.

Method D. The complex $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$ (0.20 g; 0.30 mmol) was refluxed in methanol (10 cm^3) for 3 hours. The yellow solution was filtered hot and deposited a yellow crystalline solid on cooling which was identified as $[Ru_2(\eta\text{-}C_6H_6)_2(OMe)_3]BPh_4$ (0.20 g; 90%). Similarly prepared from ethanol and $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$ was $[Ru_2(\eta\text{-}C_6H_6)_2(OEt)_3]BPh_4$.

Tri-μ-phenoxobis[η-benzeneruthenium(II)] tetraphenylborate

By method C, using [{$Ru(\eta\text{-}C_6H_6)Cl_2$}$_2$] (0.10 g; 0.20 mmol) and an excess of freshly prepared NaOPh in methanol (10 cm^3) (made from NaOMe and excess phenol in methanol). This mixture was gently heated to give a yellow solution and addition of $NaBPh_4$ (0.07 g, 0.20 mmol) gave a yellow solid which was washed with methanol and air dried (0.10 g; 52%) (m.p. 195—196°C) [ν(CO) 1065 cm^{-1}; ν(RuO) 490 cm^{-1} (mull)].

Tri-μ-methoxobis[η-benzene osmium(II)]tetraphenylborate

By method C using [{$Os(\eta\text{-}C_6H_6)Cl_2$}]$_2$ (0.10 g; 0.15 mmol) and a freshly prepared solution of NaOMe in methanol (10 cm^3). The mixture was stirred and heated gently to give a clear solution and then addition of $NaBPh_4$ (0.07 g; 0.20 mmol) gave a microcrystalline white solid which was washed with methanol and air dried (0.06 g; 39%) (m.p. 174—176°C) [ν(CO) 1048 cm^{-1}; ν(OsO) 400 cm^{-1}].

Tri-μ-methoxobis[(η-hexamethylbenzene)ruthenium(II)] tetraphenylborate

By method C using [{$Ru(\eta\text{-}C_6Me_6)Cl_2$}]$_2$ (0.10 g; 0.15 mmol) and freshly prepared NaOMe [Na (0.10 g) in MeOH (15 cm^3)]. The mixture was stirred and heated gently to give a yellow solution and addition of $NaBPh_4$ (0.07 g; 0.20 mmol) gave a yellow solid which was filtered off and washed with methanol (0.07 g; 47%) (m.p. 168—172°C) [ν(CO) 1050 cm^{-1}; ν(RuO) 495 cm^{-1} (mull)].

Tri-μ-methoxobis[(η-mesitylene)ruthenium(II)]tetraphenylborate

By method C, using [{$Ru(\eta\text{-}C_6H_3Me_3)Cl_2$}$_2$] (0.12 g; 0.20 mmol) and freshly prepared NaOMe [Na (0.10 g) in methanol (10 cm^3)]. The resulting orange solution was filtered and an excess of $NaBPh_4$ (0.20 g; 0.60 mmol) in methanol

added to give a copious yellow precipitate which was filtered and washed with methanol and diethylether (0.12 g; 65%) (m.p. 203—205°C) [ν(CO) 1025 cm^{-1}]. ^{13}C-{^1H} NMR in $(CD_3)_2CO$ (298 K): δ 121—136 ppm (BPh_4^-); δ 91.4 (*C*Me), 77.7 (*C*H), 67.2 (OMe), 17.4 (Me) ppm. Slope of $\Lambda_0 - \Lambda_e$ vs. $C_e^{1/2}$ plot in CH_3NO_2 = 176.

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PREPARATION, X-RAY CRYSTAL STRUCTURE ANALYSIS AND SOME REACTIONS OF THE HYDROXO-BRIDGED, TETRANUCLEAR, η-ARENE RUTHENIUM(II) QUADRIVALENT CATION $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4](SO_4)_2 \cdot 12\ H_2O$

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Summary

Reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with aqueous Na_2CO_3 (1 : 2 molar ratio) in the presence of an excess of Na_2SO_4 gives the cubane-like complex $[\{Ru(\eta\text{-}C_6H_6)OH\}_4](SO_4)_2 \cdot 12\ H_2O$ (A) whose structure has been determined by X-ray analysis. The crystals are cubic, space group $Pm3n$, with a = 12.405(1) Å. A possible mechanism of formation of compound A and its reactions with NaOH, LiBr, C_5H_5N, 4-MeC_5H_4N and 1,10-phenanthroline are also described.

Recently, we have presented the full results of our studies on the synthesis of binuclear hydroxo-bridged η-arene complexes of ruthenium(II) [1]. These complexes were prepared by the reaction of various $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ compounds (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6, p-$MeC_6H_4CHMe_2$) with an excess of aqueous NaOH or Na_2CO_3, followed by precipitation with $NaBPh_4$. However, if $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ is treated with less Na_2CO_3($[Ru^{2+}] : [CO_3^{2-}]$ ca. 1 : 1 molar ratio) in the presence of a large excess of Na_2SO_4, the novel tetranuclear, hydroxo-bridged, η-arene ruthenium(II) complex $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4](SO_4)_2 \cdot 12\ H_2O$ can be isolated. The full details [2] of the preparation, X-ray analysis and some reactions of this compound are now presented in this paper.

Results and discussion

As discussed earlier [1], reaction of an aqueous solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with an excess of NaOH (or Na_2CO_3) gave, on warming, a yellow solution from which a yellow solid could be precipitated by addition of $NaBPh_4$. On the basis of various physicochemical studies, this product was

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shown to be a mixture of mainly $[\eta\text{-}C_6H_6(OH)Ru(OH)_2Ru(H_2O)(\eta\text{-}C_6H_6)]BPh_4$ together with some $[\eta\text{-}C_6H_6Ru(OH)_3Ru(\eta\text{-}C_6H_6)]BPh_4$. Recrystallisation from acetone then gave pure samples of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4Me_2CO$.

If, however, $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ was dissolved in water and shaken with a large excess of Na_2SO_4 for a short period and this solution then treated with Na_2CO_3, ($[Ru^{2+}] : [CO_3^{2-}]$ ca. 1 : 1 molar ratio), an orange crystalline solid (A) was deposited in low yield. The same product was obtained if Na_2HPO_4 ($[Ru^{2+}] : [HPO_4^{2-}]$ ca. 1 : 1 molar ratio) was added but no solid was precipitated on shaking only Na_2SO_4 with $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ for prolonged periods. The yield of compound A could be considerably increased by pretreating an aqueous solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $AgNO_3$ and, after filtering off the AgCl, shaking with an excess of Na_2SO_4 followed by Na_2CO_3 (1 : 2 molar ratio).

Unfortunately, compound A was too insoluble in organic solvents for ^1H NMR studies and too involatile for mass spectral studies. The mull IR spectrum of A showed very broad bands at ca. 3250 and 1640 cm^{-1} assigned to the ν(OH) and δ(HOH) vibrational modes of water and these of course obscured any ν(OH) bands arising from hydroxo groups (cf. $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OH)_3]Cl \cdot 3\,H_2O$ [1]). No bands due to ν(RuCl) vibrations were observed in the IR spectrum but bands at 1060, 975, 610 and 478 cm^{-1} suggested the presence of sulphate ion [3] and a strong band at 864 cm^{-1} indicated retention of the benzene ring.

The compound was very sparingly soluble in water and gave strongly conducting solutions. Furthermore, freeze-drying of an aqueous solution of A produced a solid with the same properties as A, indicating that dissociation of this complex to form ions was not caused by decomposition in water. A solid could be precipitated on addition of $NaBPh_4$ to this aqueous solution but this rapidly decomposed on standing for short periods.

Elemental analyses on A confirmed the presence of C, H, O, and S and the absence of chlorine and suggested the empirical formula $C_{12}H_{26}O_{12}Ru_2S$, which, together with the information given above, suggested the molecular formula $[Ru(\eta\text{-}C_6H_6)OH]_{2n}(SO_4)_n \cdot 6n\,H_2O$. Fortunately, the orange crystalline solid (A) was suitable for X-ray structural analysis (see below) and this showed it to be the unusual $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4](SO_4)_2 \cdot 12\,H_2O$ complex containing π-bonded benzene groups and hydroxo bridges.

Crystal Data for A. $[Ru_4(C_6H_6)_4(OH)_4]^{4+}$, 2 SO_4^{2-}, 12 H_2O ($C_{24}H_{52}O_{24}Ru_4S_2$), M = 1193, dark red octahedra, cubic, a = 12.405(1) Å, U = 1909 Å^3, D_m = 2.10, Z = 2, D_c = 2.08 g cm^{-3}, μ(Mo-K_α) = 17.1 cm^{-1}, space group $Pn3m$ (no 224), conditions for reflection, $hk0$, $h0l$, $0kl$, $h + k + l = 2n$).

Refinement of Crystal Structure of A. Data collection is described in the Experimental section. The approximate parameters, reported previously, [2], were refined with careful constraints, in view of the extensive disorder. The final values, together with site symmetries and site occupancies, are given in Table 1.

In the cation, which is centred at 1/4, 1/4, 1/4 and has $\bar{4}3m$ (T_d) symmetry, the Ru and O atoms were refined anisotropically, (a total of 6 parameters). The coordinated benzene is disordered over two positions, related by a 30° rotation about a threefold axis. These rings were given fixed site occupancies of 0.5 and

TABLE 1

CRYSTAL PARAMETERS FOR A.

See text for discussion of errors.

Atom	Site symmetry		Site occupancy	10^4X	10^4Y	10^4Z	$10^4U(Å^2)$	$10^4U_{ij}(Å^2)$
Ru	$3m$	C_{3v}	1.0	1558	1558	1558	246	−37
O(1)	$3m$	$C3_v$	1.0	3241	3241	3241	244	−32
C(1)	1	C_1	0.5	−2	803	1608	327	—
C(2)	m	C_s	0.5	338	338	1733	442	—
C(3)	m	C_s	0.5	1268	1268	−127	436	—
S	$3m$	C_{3v}	0.5	5092	5092	5092	1549	−972
O(2)	$3m$	C_{3v}	0.5	4405	4405	4405	546	—
O(3)	m	C_s	0.5	5783	5783	4405	3371	—
$H_2O(1)$	222	D_2	0.5	0	2500	7500	2327	—
$H_2O(2)$	m	C_s	0.5	1438	1438	7104	2610	—
$H_2O(3)$	$\bar{4}2m$	D_{2d}	0.5	2500	2500	7500	3161	—

were constrained to be identical regular hexagons, normal to the threefold axis. One ring consists of 6 symmetry related atoms in general positions [C(1)] while the other has two groups of 3 symmetry related atoms on mirror planes [C(2) and C(3)]. The constraints for the carbon atoms may be expressed thus: C(1) at $u - v$, u, $u + v$; C(2) at $u - w$, $u - w$, $u + 2w$; C(3) at $u + w$, $u + w$, $u - 2w$. In the refined structure, $u = 0.0803$, $v = w\sqrt{3} = 0.0805$. Hydrogen atoms for the benzene ring and for the hydroxyl group were included in the refinement in fixed positions to give C—H = 1.10 Å, O—H = 1.02 Å. The standard deviations for the four positional parameters are: xyz[Ru]; 0.0008 Å, xyz[O(1)]: 0.007 Å, u: 0.006 Å, v: 0.006 Å.

The sulphate ions are disordered about $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with averaged symmetry $3m(D_{3d})$. The sulphur atom and the oxygen lying along the threefold axis have essentially twofold disorder, while the position of the other atoms is much less well defined. For refinement, the ions were constrained to be a set of interpenetrating regular tetrahedra with S—O fixed at 1.48 Å. The high temperature factor of O(3) and some residual electron density in the vicinity shows that the model is not entirely adequate. The standard deviation of xyz[S], the only positional parameter refined, is 0.013 Å.

The water molecules are very poorly defined. Their presence is indicated by elemental analysis and the X-ray molecular weight, but they only show on difference electron density syntheses as broad peaks in the channels intersecting at 1/4, 1/4, 3/4 and symmetry related positions, with $\bar{4}2m(D_{2d})$ symmetry. Various positions were tried, but the best refinement occurred with half occupancy of three independent sites. This accounts for $10\frac{1}{2}$ of the 12 water molecules required by the formula, but can only be taken as an approximate indication of the positions occupied by water molecules in the crystal. The root mean square standard deviation of H_2O (2) is 0.06 Å.

A projection of one cation along a $\bar{4}$ (S_4) axis is shown in Fig. 1. The Ru—O distance in the "cube" is 2.117(7) Å, and the angles at Ru and O are 75.8(1)° and 102.6(2)°, respectively. The centres of the benzene rings are 1.622(8) Å from the ruthenium atoms, and the Ru—C distance is 2.151(8) Å. The C—C dis-

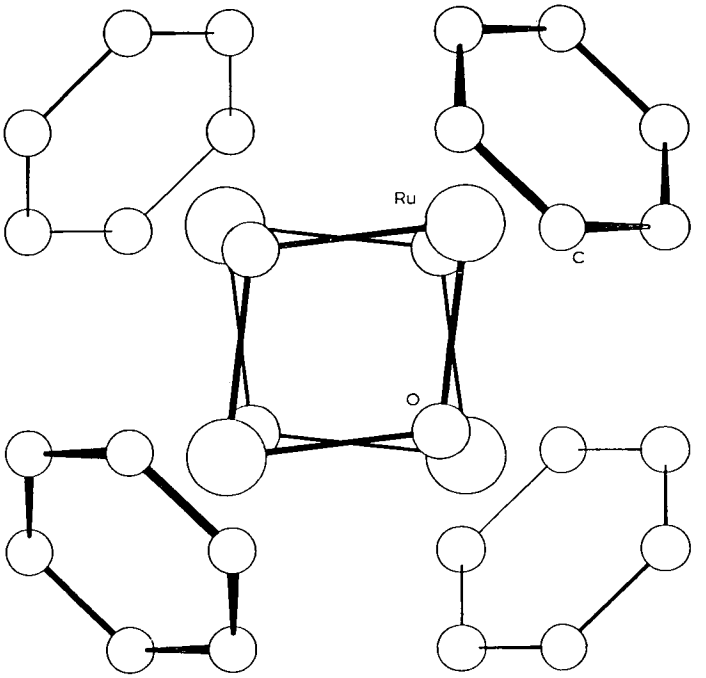


Fig. 1. Projection of $[\{Ru(\eta\text{-}C_6H_6)OH\}_4]^{4+}$ cation along a $\bar{4}$ (S_4) axis.

tance in the rings is 1.395(10) Å. This tetrameric cation is, to our knowledge, only the second ruthenium complex with this cubane stereochemistry ($[Ru_4(\eta^5\text{-}C_5H_5)_4(\mu_3\text{-}CO)_4]$ is the other [4]) and the first example of a cubane-like structure containing π-bonded arene rings. A large number of cubane clusters containing a wide range of elements, bridging and terminal groups have however been synthesised [5].

Unfortunately, attempts to synthesise other $[\{Ru(\eta\text{-arene})OH\}_4]^{4+}$ cations by reaction of $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$, p-MeC_6H_4-$CHMe_2$) with stoichiometric amounts of Na_2CO_3 in the presence of an excess of Na_2SO_4 in water were unsuccessful since only unreacted starting materials and/or the triple hydroxo-bridged cations $[Ru_2(\eta\text{-arene})_2(OH)_3]^+$ were recovered on work-up. For example, treatment of either $[\{Ru(\eta\text{-}C_6H_3Me_3)Cl_2\}_2]$ or $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ with aqueous $AgNO_3$ followed by shaking with an excess of Na_2SO_4 and then Na_2CO_3 (1 : 2 molar ratio) for several hours gave on concentration, the triple hydroxo-bridged complexes $[Ru_2(\eta\text{-}C_6H_3Me_3)_2(OH)_3]$-$NO_3 \cdot H_2O$ and $[Rh_2(\eta\text{-}C_5Me_5)_2(OH)_3]NO_3 \cdot 2\,H_2O$, respectively.

The crystal structure gives an indication as to why arenes other than benzene do not form similar complexes. Each cation in A may be regarded as being bonded to eight others through the cube corners. At the vertices occupied by Ru, this is achieved by strong Van der Waals interactions between the benzene rings of adjacent cations. These lie in parallel planes separated by 3.45 Å (cf. 3.35 Å in graphite). This close approach implies that the rings are staggered with respect to one another (C···C = 3.53 Å) but such local ordering will have

no effect on the relative positions of pairs of benzene rings elsewhere in the structure. At the same time, the vertices of the cube occupied by OH are hydrogen bonded to the sulphate ion lying between them. In whichever way it is oriented, an atom of type O(2) will lie 2.50 Å from the O(1) of one cube, while the three atoms of type O(3) will be 3.38 Å from the O(1) of another. Thus the stability of the crystal, and probably of the cation, depends both on the arenes having no aliphatic substituents and the anions being of suitable size to bridge a gap between two OH groups for which O···O is 7.56 Å and H···H is about 5.50 Å.

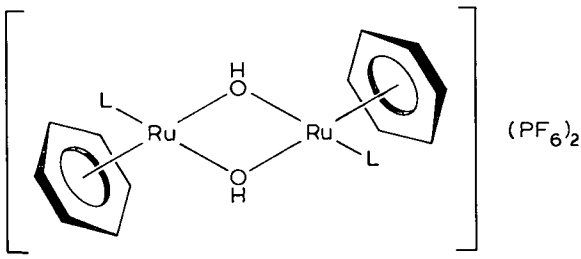
A possible mechanism of formation of compound A is via deprotonation of the trisaqua cation $[Ru(\eta\text{-}C_6H_6)(H_2O)_3]^{2+}$ (generated in situ in high yield by reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with aqueous $AgNO_3$ [6]) by equimolar amounts of CO_3^{2-} or HPO_4^{2-} to give the $[Ru(\eta\text{-}C_6H_6)(H_2O)_2OH]^+$ cation. The combination of the bridging propensity of hydroxo groups and the desire of ruthenium(II) to exhibit six coordination [7] could then lead to tetramerisation of the $[Ru(\eta\text{-}C_6H_6)(H_2O)_2OH]^+$ cation with concomitant elimination of water to form the $[\{Ru(\eta\text{-}C_6H_6)OH\}_4]^{4+}$ cubane cluster cation. This process is enhanced by the presence of an excess of sulphate ion which removes the tetrameric cation from solution. In fact, if an aqueous solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ was treated with an equimolar amount of Na_2CO_3 before addition of Na_2SO_4, then only binuclear hydroxo-bridged cations (see ref. [1]) could be isolated from the solution.

In support of this observation, treatment of compound A with either aqueous Na_2CO_3 or NaOH followed by addition of $NaBPh_4$ readily gave $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]BPh_4 \cdot H_2O$. The ^1H NMR spectrum of this compound in $(CD_3)_2CO$ at 298 K showed only one $\eta\text{-}C_6H_6$ resonance at δ 5.60 ppm which indicated that no $[\eta\text{-}C_6H_6(OH)Ru(OH)_2Ru(H_2O)(\eta\text{-}C_6H_6)]BPh_4$ ([δ 5.33 ppm (^1H NMR)] [1]) had been formed by this route. Hence, the tetrameric $[\{Ru(C_6H_6)(OH)\}_4]^{4+}$ cation is readily cleaved by hydroxide ion to give the binuclear $[Ru_2(C_6H_6)_2(OH)_3]^+$ cation.

Similarly, treatment of compound A with aqueous LiBr (1 : 2 molar ratio) gave an orange solution from which orange-yellow solids could be precipitated by addition of either NH_4PF_6 or $NaBPh_4$. These compounds analysed quite closely for "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_2Br]Y$" ($Y = PF_6^-$, BPh_4^-) but their ^1H NMR spectra contained several $\eta\text{-}C_6H_6$ resonances. A possible explanation of this observation is that in solution the $(\mu\text{-}OH)_2(\mu\text{-}Br)$ cation rapidly rearranged to give a mixture containing the $(\mu\text{-}OH)_3$, $(\mu\text{-}OH)_2(\mu\text{-}Br)$, $(\mu\text{-}OH)(\mu\text{-}Br_2)$ and $(\mu\text{-}Br)_3$ cations (cf. related studies on the "$[Ru_2(\eta\text{-}C_6H_6)_2Cl_2Br]^+$" and "$[Ru_2(\eta\text{-}C_6H_6)_2ClBr_2]^+$" cations [8]. The same species were obtained on mixing nitromethane solutions of $[Ru_2(\eta\text{-}C_6H_6)_2(OH)_3]^+$ and $[Ru_2(\eta\text{-}C_6H_6)_2Br_3]^+$ cations. On leaving in solution the "$[Ru_2(\eta\text{-}C_6H_6)_2(OH)_2Br]^+$" cation slowly deposits some insoluble $[\{Ru(\eta\text{-}C_6H_6)Br_2\}_2]$ and this was the only product formed when compound A was treated with an excess of LiBr.

Similarly, compound A reacted in water with neutral Lewis bases such as pyridine and 4-methylpyridine (L) to give yellow solutions from which yellow solids were precipitated on addition of NH_4PF_6. These however were formulated as the dicationic, binuclear complexes $[\{Ru(\eta\text{-}C_6H_6)OHL\}_2](PF_6)_2$ (I) on the basis of elemental analyses, ^1H NMR, IR and conductivity studies. Again,

cleavage of the tetramer has occurred but since pyridine and 4-methylpyridine do not act as bridging groups, the double hydroxo-bridged cation (I) was produced.



(I)

Finally, compound A reacted with an excess of 1,10-phenanthroline in water under reflux to give an orange solution from which an orange solid was precipitated by addition of NH_4PF_6. This did not contain any η-benzene or hydroxo groups and was formulated as the previously known $[Ru(phen)_3](PF_6)_2$ [9].

Experimental

Microanalyses were by BMAC and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000—250 cm^{-1} on a Perkin-Elmer 447 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1-NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers. Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate, rhodium trichloride and silver nitrate (Johnson Matthey Ltd), CD_3NO_2, cyclohexa-1,3-diene, NH_4PF_6 (Aldrich Chemicals); pyridine (Fisons), 1,10-phenanthroline (BDH). The compounds $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ [8] and $[\{Rh(\eta\text{-}C_5H_5)Cl_2\}_2]$ [10] were prepared as described elsewhere.

Tetra-μ_3-hydroxotetrakis[(η-benzene)ruthenium(II)] sulphate hydrate (1/12). The complex $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.20 g; 0.40 mmol) was dissolved in water (10 cm^3) and the orange solution was filtered. An excess of Na_2SO_4 (0.20 g, 1.50 mmol) was then added, the solution shaken vigorously for 10 minutes and then Na_2CO_3 (0.08 g; 0.80 mmol) added. On further vigorous shaking for 24 hours, the orange crystalline solid was deposited from solution, m.p. 200°C (decomp) (0.07 g; 31%). Alternatively, an aqueous solution of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.20 g; 0.40 mmol) in water (10 cm^3) was shaken with $AgNO_3$ (0.27 g; 1.60 mmol). After filtering off the AgCl, the orange/yellow solution was treated as above with Na_2SO_4 (0.20 g; 1.50 mmol) and then Na_2CO_3 (0.08 g; 0.80 mmol) to give orange crystals (0.14 g; 60%) [ν(OH) 3250 cm^{-1}; δ(HOH) 1640 cm^{-1}; ν(S—O) 1060, 610, 975 and 478 cm^{-1}] Found: C, 24.4; H, 3.9; O, 30.4; S, 4.7. Calcd. for $C_{24}H_{52}O_{24}S_2Ru_4$: C, 24.2; H, 4.4; O,

32.2; S, 5.4%. Λ_m (10^{-3} mol dm^{-3}) in water = 198 S cm^2 mol^{-1}.

The same compound was also prepared by using Na_2HPO_4 (0.11 g; 0.80 mmol) instead of Na_2CO_3.

Tri-μ-hydroxobis[(η-mesitylene)ruthenium(II)] nitrate hydrate (1/1). The complex [{Ru(η-$C_6H_3Me_3$)Cl_2}$_2$] (0.23 g; 0.40 mmol) was dissolved in water (15 cm^3) by refluxing and $AgNO_3$ (0.27 g; 1.60 mmol) added. The AgCl precipitate was filtered off and the yellow filtrate was shaken with an excess of Na_2SO_4 (0.20 g; 1.50 mmol) and then Na_2CO_3 (0.08 g; 0.40 mmol) for ca. 2 hours. The solution was then concentrated under vacuo to give a yellow crystalline solid, m.p. 195°C (decomp) (0.06 g; 25%) [ν(OH) 3250(br) cm^{-1}, δ(HOH) 1650 cm^{-1}; ν(NO) 1045, 830, 720 cm^{-1}] Found: C, 38.6, H, 4.8; N, 2.5. Calcd. for $C_{18}H_{29}NO_7Ru_2$: C, 37.7; H, 5.1; N, 2.4% [Λ_m (10^{-3} mol dm^{-3}) in water = 69 S cm^2 mol^{-1}] ^{1}H NMR in D_2O (external Me_4Si capillary reference) at 298 K: 5.30 (s) (H); 2.50 (s) (Me).

Addition of $NaBPh_4$ to an aqueous solution of [Ru_2(η-$C_6H_3Me_3$)$_2$$(OH)_3$]-$NO_3$ · H_2O gave [Ru_2($C_6H_3Me_3$)$_2$$(OH)_3$]$BPh_4$.

Tri-μ-hydroxobis[pentamethyl(cyclopentadienyl)rhodium(III)] nitrate hydrate (1/2). This was prepared by the same method as [Ru_2($C_6H_3Me_3$)$_2$$(OH)_3$]-$NO_3$ · H_2O starting from [{Rh(η-C_5Me_5)Cl_2}$_2$], m.p. 165°C (decomp) (60%) [ν(OH) 3250 cm^{-1}; δ(HOH) 1660 cm^{-1}; ν(NO) 1030, 830, 720 cm^{-1}] Found: C, 38.3; H, 5.5; N, 2.2. Calcd. for $C_{20}H_{37}NO_8Rh_2$: C, 38.4, H, 5.9; N, 2.2%].

Tri-μ-hydroxobis[(η-benzene)ruthenium(II)] tetraphenylborate hydrate (1/1). The compound [{Ru(η-C_6H_6)OH}$_4$]$(SO_4)_2$ · 12 H_2O (0.10 g; 0.08 mmol) was added to NaOH (0.15 g; 4.0 mmol) dissolved in water (5 cm^3). The solution was warmed gently and an orange precipitate formed. This was filtered off, redissolved in water and addition of $NaBPh_4$ then gave an orange-yellow precipitate, m.p. 195°C (decomp) (0.04 g; 34%) [ν(OH) 3620, 3500 cm^{-1}; ν(OH)-(H_2O) 3220 cm^{-1}; δ(HOH) 1620 cm^{-1}] Found: C, 58.9; H, 4.8. Calcd. for $C_{36}H_{37}BO_4Ru_2$: C, 57.9, H, 5.0%] ^{1}H NMR in $(CD_3)_2CO$ at 298 K: 5.60 (s) (η-C_6H_6); 6.90—7.60 (m) (BPh_4^-).

"μ-Bromo(di-μ-hydroxo)bis[(η-benzene)ruthenium(II)] hexafluorophosphate hydrate (1/2)". The complex [{Ru(η-C_6H_6)OH}$_4$]$(SO_4)_2$ · 12 H_2O (0.10 g; 0.08 mmol) was suspended in water and LiBr (0.015 g; 0.16 mmol) was added giving an orange solution. Addition of NH_4PF_6 (0.05 g; 0.40 mmol) gave an orange-yellow precipitate, m.p. 170°C (decomp) (0.05 g; 51%) [ν(OH) 3640, 3580 cm^{-1}; ν(OH)(H_2O) 3300 cm^{-1}; δ(HOH) 1630 cm^{-1}] Found: C, 21.6; H, 2.4; Br, 12.9. Calcd, for "$C_{12}H_{18}BrF_6O_4PRu_2$": C, 22.0; H, 2.7; Br, 12.3%.

"μ-Bromo(di-μ-hydroxo)bis[(η-benzene)ruthenium(II)] tetraphenylborate was similarly prepared from [{Ru(η-C_6H_6)OH}$_4$]$(SO_4)_2$ · 12 H_2O, LiBr and $NaBPh_4$. [Found: C, 54.8; H, 4.4. Calcd. for "$C_{36}H_{34}BBrO_2Ru_2$": C, 54.6; H, 4.3%] ^{1}H NMR in $(CD_3)_2CO$ at 298 K: 5.92 (s) (-(μ-Br_3)-); 5.88 (s) (-(μ-OH)-(μ-Br_2)-); 5.70 (s) (-(μ-OH_2)(μ-Br)-; 5.52 (s) (-(μ-$(OH)_3$)-; 6.90—7.60 (m) (BPh_4^-).

Di-μ-hydroxobis[(η-benzene)pyridineruthenium(II)] hexafluorophosphate. The complex [{Ru(η-C_6H_6)OH}$_4$]$(SO_4)_2$ · 12 H_2O (0.10 g; 0.08 mmol) was suspended in water and pyridine (0.50 cm^3) was added. The solution was gently warmed and addition of NH_4PF_6 to the resulting yellow solution gave a yellow

precipitate, m.p. 205°C (decomp) (0.09 g; 68%) [ν(OH) 3640, 3590 cm^{-1}] [Found: C, 31.4, H, 2.9; N, 3.5. Calcd: for $C_{22}H_{24}F_6N_2O_2PRu_2$: C, 31.4; H, 2.9; N, 3.3%).] Λ_m (10^{-3} mol dm^{-3}) in CH_3NO_2 = 176 S cm^2 mol^{-1}. ^1H NMR in $(CD_3)_2CO$ at 298 K 2.05 (s) (OH^-); 5.88 (s) (η-C_6H_6), 7.10 (m), 8.30 (m) (C_5H_5N). Similarly prepared was di-μ-hydroxobis[(η-benzene)(4-methylpyridine)ruthenium(II)] hexafluorophosphate, m.p. 195°C (decomp.) (0.09 g, 65%) [ν(OH) 3650, 3590 cm^{-1}]. [Found: C, 32.9; H, 3.2; N, 3.3. Calcd. for $C_{24}H_{28}F_6N_2O_2PRu_2$: C, 33.2; H, 3.2; N, 3.2%] [Λ_m (10^{-3} mol dm^{-3}) in CH_3NO_2 = 150 S cm^2 mol^{-1}]. ^1H NMR in $(CD_3)_2CO$ at 298 K: 2.45 (s) (OH^-); 5.88 (s) (η-C_6H_6); 2.31 (s) (Me), 6.90 (d); 8.05 (d) (MeC_5H_4N).

Tris(1,10-phenanthroline)ruthenium(II) hexafluorophosphate diethyletherate (1/1). The complex $[\{Ru(\eta\text{-}C_6H_6)OH\}_4](SO_4)_2 \cdot 12\ H_2O$ (0.10 g; 0.08 mmol) was suspended in water (10 cm^3) and an excess of 1,10-phenanthroline (0.20 g; 2.0 mmol) added. The solution was refluxed for 30 min, filtered and addition of NH_4PF_6 then gave an orange solid which was recrystallised from acetone/diethyl ether, m.p. >290°C (decomp.) (0.20 g, 70%) [Found: C, 45.6; H, 3.0; N, 7.9. Calcd. for $C_{40}H_{34}F_{12}N_6OP_2Ru$: C, 45.3; H, 3.2; N, 7.9%] [Λ_m (10^{-3} mol dm^{-3}) in CH_3NO_2 = 161 S cm^2 mol^{-1}]. ^1H NMR in $(CD_3)_2CO$ at 298 K: 7.72 (m), 8.43 (m), 8.75 (m), 8.85 (m) (1,10-phen).

Crystal structure determination of A. Cell dimensions and intensity data were measured on an Enraf-Nonius CAD-4 diffractometer using monochromatised Mo-K_α radiation (λ = 0.71069 Å). The cell was refined using 24 reflections equivalent to 1, 6, 11 (2θ = 51.30°). In view of the extensive disorder reported previously [2], a more extensive data set was collected and the refinement reported here was based on it. Intensities were measured for 1741 reflections to 2θ = 70°, and these were reduced to 416 independent data including 48 systematic absences. The merging gave an estimated R-factor of 0.043 and no indication of deviation from cubic symmetry. No absorption corrections were made; the crystal used for data collection was an octahedron of edge 0.05 mm. Refinement was based on the 245 reflections with $I \geqslant 3\sigma(I)$. To rule out the possibility of the space group being $F43c$ (with a = 24.81 Å) all reflections of type uuu in that cell with $2\theta \leqslant 30°$ were measured and none gave $I > \sigma(I)$. The refinement is described in the main part of the text. For the final cycles, a weighting scheme of W = 1.0 for F_0 100, $W^{1/2} = 100/F_0$ otherwise was used. At convergence, based on 22 adjustable parameters, R = 0.048, R_w = 0.058. An analysis of agreement showed good uniformity except for reflections with low sin θ values, where the poor modelling of the disordered water would be most serious. A table of observed and calculated structure factors may be obtained on request from the authors. Crystallographic calculations made use of the SHELX and XRAY program systems [11].

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SYNTHESIS AND CHARACTERISATION OF THE MIXED SANDWICH CATIONS $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ (M = Ru, Os)

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Summary

The published reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ has been extended to other $[\{M(\eta\text{-arene})Cl_2\}_2]$ complexes to provide a convenient, high yield route to the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru; arene = C_6H_6, p-$MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M = Os; arene = C_6H_6, p-$MeC_6H_4CHMe_2$). Electrochemical studies and some reactions of these complexes are also described.

Since the preparation of the first mixed sandwich iron cation $[Fe(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_5H_5)]I$ by Coffield et al. in 1957 [1], a large number of publications on the synthesis and reactions of $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations have appeared in the literature [2].

In contrast, very few papers on the synthesis and reactions of their ruthenium and osmium analogues have been published. These consist of a very brief patent report on the preparation of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru, Os) via reaction of $[M(\eta\text{-}C_5H_5)(CO)_2]^+$ cations with the appropriate arene [3]; the synthesis of $[Ru(\eta^6\text{-}C_6H_5BPh_3)(\eta\text{-}C_5H_5)]$ via reaction of $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl]$ with $Na[BPh_4]$ [4]; a brief mention of the reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ [5] and two recent preliminary notes [6,7] on the use of the well-known Nesmeyanov route ($M(C_5H_5)_2$, $AlCl_3$, Al, arene [2]) to synthesise various $[Ru(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations. Unfortunately, using ruthenocene the latter method requires long reaction times, high temperatures and only low yields are obtained (<10% in ref. 7). These yields can be increased to 30% (for arene = 1,3,5-$C_6H_3Me_3$) by addition of water to the reaction mixture [6] but with C_6Me_6 this also results in extensive demethylation and disproportionation of the aromatic ligand. Therefore, in this short paper we now report the results of an extension of Zelonka and Baird's route [5] to the synthesis of a series of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru; arene = C_6H_6, p-$MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M = Os; arene = C_6H_6, p-

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$MeC_6H_4CHMe_2$) and also the electrochemical behaviour and some reactions [8] of these complexes.

Results and discussion

In 1972, Zelonka and Baird [5] briefly reported that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ in MeCN at ambient temperature gave a high yield (83%) of $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$. In view of the ready availability of other $[\{M(\eta\text{-arene})Cl_2\}_2]$ (M = Ru, Os) compounds [9], coupled with the alternative high temperature, low yield, Nesmeyanov route [6,7] we decided to investigate the possibility of synthesising a series of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations by reaction of $[\{M(\eta\text{-arene})Cl_2\}_2]$ with $Tl[C_5H_5]$.

Thus, reaction of $[\{M(\eta\text{-arene})Cl_2\}_2]$ with $Tl[C_5H_5]$ (1 : 2 molar ratio) in MeCN for several hours at ambient temperature gave a fine precipitate of TlCl which was removed by filtering through celite. Removal of solvent and treatment of the resulting solid or oil with a methanolic solution of $Na[BPh_4]$ produced the desired $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]BPh_4$ as greyish-white or pale brown solids. In the $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ reaction, treatment of the residue with a methanolic solution of $NH_4[PF_6]$ gave $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$ (cf. $[Ru(\eta\text{-}C_6H_6)Cl(NH_3)_2]_3(PF_6)_3NH_4PF_6$ [10]. For M = Ru, yields of 50—80% were obtained; for M = Os, lower yields of 20—40% were realised (see Experimental section). The compounds were characterised by elemental analyses, hydrogen-1 NMR (Table 1) and carbon-13 NMR (Table 2) spectroscopy and by conductivity measurements in $(CH_3)_2SO$ or CH_3NO_2.

As reported earlier for Fe and Ru analogues [7], the $\eta\text{-}C_5H_5$ protons shift to higher frequencies on descending the triad, e.g. for the $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cations, M = Fe, δ 5.23 [7]; M = Ru, 5.43; M = Os, 5.67 ppm. Conversely, the

TABLE 1

HYDROGEN-1 NMR DATA AT 301 K IN $(CD_3)_2SO$ FOR SOME $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ CATIONS (M = Ru, Os)

Compound	δ (ppm) [a, b]	
	η-arene	$\eta\text{-}C_5H_5$
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$	6.20(s)	5.43(s)
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c]	6.11s, 4 H); 2.22(s, CH_3); 1.15(d, CH_3 of $CHMe_2$, J 6.0 Hz)	5.31(s)
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)]BPh_4$	5.80—6.50(m, 5 H) 3.67(s, OMe)	5.34(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$ [d]	2.39(s)	4.96(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	2.33(s)	5.09(s)
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]BPh_4$	6.14(s)	5.67(s)
$[Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c, d]	6.15(s, 4 H) 2.43(s, CH_3) 1.24(d, CH_3 of $CHMe_2$, J 6.0 Hz)	5.59(s)

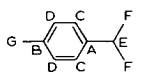
[a] Reference standard-internal Me_4Si lock. [b] Where appropriate BPh_4^- multiplets observed between δ 6.60—7.60 ppm. [c] $CHMe_2$ septet not observed due to low solubility of compound. [d] Measured in CD_3NO_2.

TABLE 2

CARBON-13 NMR DATA (PROTON NOISE DECOUPLED) AT 301 K IN $(CD_3)_2SO$ FOR SOME $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ CATIONS

Compound	δ ppm [a, b]	
	η-arene	η-C_5H_5
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6)_2NH_4PF_6$	85.8	80.9
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c]	111.7(A), 100.7(B) 86.0(C), 84.0(D), 31.2(E), 23.1(F), 19.6(G)	80.3
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)]BPh_4$	(85.8, 84.1, 82.9 80.0, 74.4) [d], 57.1 [e]	79.6
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]BPh_4$	76.1; 76.5 [f]	
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	98.9 [g], 17.3 [h]	81.6

[a] Chemical shifts quoted to high frequency of $SiMe_4$ (internal lock). [b] Where appropriate BPh_4^- resonances observed between δ 120—140 ppm. [c] Labelling of *p*-cymene protons



[d] Aromatic carbons of C_6H_5OMe. [e] Methyl carbon of C_6H_5OMe. [f] Not possible to assign resonances unambiguously as they are so close together and similar in intensity. [g] Aromatic carbons of C_6Me_6. [h] Methyl carbons of C_6Me_6.

benzene protons shift to lower frequency, e.g. for the $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cations, M = Fe δ 6.44 [7]; M = Ru, 6.20; M = Os, 6.14 ppm. As suggested earlier [7], this might indicate that the positive charge of the cations is delocalised onto the arene ligand in the order Fe > Ru > Os.

In support of this statement, attempted reactions of some of these $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations with various nucleophiles (Y) gave either no reaction (M = Ru; Y = various PR_3; M = Os, Y = various PR_3, H^-, CN^-, OH^-) or extensive decomposition which probably involved displacement of both carbocyclic rings (M = Ru; Y = CN^-, OH^-). This behaviour is to be contrasted with that of the $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations which react readily with various nucleophiles to give high yields of *exo*-substituted cyclohexadienyl complexes, $[Fe(\eta\text{-}C_6R_6Y)(\eta\text{-}C_5H_5)]$ etc. [2]. The only evidence we have found for nucleophilic attack on the arene ring occurred in the reaction of the $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cation with $Na[BH_4]$ in 1,2-dimethoxyethane from which $[Ru(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ could be isolated in very small yield (ca. 5%) by extraction with petroleum ether (b.p. 60—80°C). This compound exhibited a very similar hydrogen-1 NMR spectrum [11] and mass spectral fragmentation pattern [12] (see Experimental section) to that of $[Fe(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$.

A similar reduction of reactivity towards tertiary phosphines in the order Fe >> Ru > Os has been observed in the series $[M(\eta\text{-}C_6H_6)_2](PF_6)_2$, and this has been attributed to the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II} [13].

Finally, in view of the extensive studies on the electroreduction of various $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations [14], an electrochemical study was carried out on the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]BPh_4$ complexes. However, unlike the iron compounds, cyclic voltammetric and A.C. polarographic studies in CH_3NO_2 or

CH_3CN showed that all the ruthenium and osmium mixed sandwich compounds studied (see Experimental section) resisted reduction upto the solvent limit. The complexes $[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$, $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$ and $[Os(\eta\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ did undergo oxidation at fairly modest potentials (see Experimental section) (unlike $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]PF_6$, which showed no oxidation wave upto the solvent limit) but unfortunately these processes remained irreversible in nature even at low temperatures (—40°C) and high scan rates (100 V s^{-1}).

It is likely that these disappointing electrochemical observations can also be correlated with the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II}.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000—250 cm^{-1} on a Perkin Elmer 447 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and $^{13}C\text{-}\{^1H\}$ NMR spectra on a Varian CFT-20 spectrometer operating at 20 MHz (^{13}C NMR chemical shifts quoted in ppm to high frequency of tetramethylsilane). Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. The mass spectrum of $[Ru(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ was measured on an A.E.I. MS9 spectrometer. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate, sodium hexachloroosmate(IV) (Johnson-Matthey Ltd.), ammonium hexafluorophosphate, dicyclopentadiene, cyclohexa-1,3-diene (Aldrich Chemicals), α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) (Eastman Chemicals), sodium tetraphenylborate, thallium(I)-sulphate (BDH). Various cyclohexa-1,4-dienes were prepared by the Birch reduction of the corresponding arene [15] and then $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, C_6H_5OMe, $p\text{-}MeC_6H_4CHMe_2$) and $[\{Os(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$) were prepared as described elsewhere [9]. The compound $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ was prepared by direct exchange of $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ with C_6Me_6 [16]. Thallium(I) cyclopentadienide was prepared from freshly cracked cyclopentadiene and thallium(I) sulphate [17].

Hydrogen-1 NMR and carbon-13 NMR data are given in Tables 1 and 2 respectively. All reactions were carried out in degassed solvents under an atmosphere of nitrogen.

Bis[η-benzene-η-cyclopentadienylruthenium(II) hexafluorophosphate](2/1)-[ammonium hexafluorophosphate]

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.30 g; 0.60 mmol) was dissolved in acetonitrile (80 cm^3) and $Tl[C_5H_5]$ (0.32 g; 1.17 mmol) was added. The reaction mixture was stirred under nitrogen for four hours. The precipitated thallium(I) chloride was removed by filtration through celite. The resulting

orange solution was evaporated to dryness on a rotary evaporator and the orange-brown residue redissolved in a small amount of methanol (3 cm^3). Addition of an excesss of $NH_4[PF_6]$ precipitated a light brown solid, m.p. 110—112°C (yield 0.28 g; 60%). Found: C, 29.3; H, 2.9; N, 1.5. Calcd. for $C_{22}H_{26}F_{18}NP_3Ru_2$; C, 28.1; H, 2.8; N, 1.5%. Λ_m (10^{-3} mol dm^{-3} in $(CH_3)_2SO$ at 303 K) = 40 S cm^2 mol^{-1}.

η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienylruthenium(II) tetraphenylborate

The compound $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.30 g; 0.49 mmol) was dissolved in acetonitrile (80 cm^3) and $Tl[C_5H_5]$ (0.29 g; 1.06 mmol) was added. The reaction mixture was stirred under nitrogen for two hours. The precipitated thallium(I) chloride was removed by filtration through celite and the resulting solution evaporated to dryness. The orange-brown residue was redissolved in methanol (3 cm^{-1}) and an excess of $Na[BPh_4]$ (0.20 g; 0.58 mmol) added to produce a pale greyish-brown precipitate which was filtered off, washed with methanol and diethyl ether and dried in vacuo at 56°C, m.p. 168—169°C (decomp.) (0.51 g; 82%) Found: C, 75.6; H, 6.5. Calcd. for $C_{39}H_{39}BRu$: C, 75.6; H, 6.3%.

η-Methoxobenzene-η-cyclopentadienylruthenium(II) tetraphenylborate (m.p. 123—125°C (0.26 g; 47%). Found: C, 72.1; H, 5.5 (calcd. for $C_{36}H_{33}BORu$: C, 74.8; H, 5.7%) and η-hexamethylbenzene-η-cyclopentadienylruthenium(II) tetraphenylborate (m.p. 252°C (decomp.) (0.15 g; 64%). Found: C, 75.8; H, 6.8 (calcd. for $C_{41}H_{43}BRu$: C, 76.0; H, 6.7%. Λ_m (10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 51 S cm^2 mol^{-1}) were also synthesised from the corresponding $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ and $Tl[C_5H_5]$ followed by treatment with $Na[BPh_4]$. An impure sample of $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$ (contaminated with excess TlCl) was also characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (see Tables 1 and 2).

η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienylosmium(II) tetraphenylborate

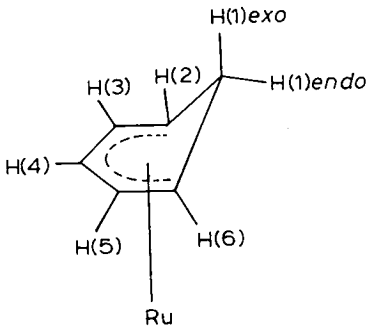
The compound $[\{Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.16 g; 0.20 mmol) was suspended in acetonitrile (50 cm^3) and $Tl[C_5H_5]$ (0.22 g; 0.82 mmol) was added. The reaction mixture was stirred under nitrogen for two hours and then filtered through celite to remove thallium(I) chloride. Removal of solvent gave a yellowish oil which was dissolved in methanol (3 cm^3) and treated with $Na[BPh_4]$ (0.20 g; 0.58 mmol) to give a greyish-white precipitate. This was filtered off, washed with methanol, chloroform and diethyl ether and dried in vacuo at 56°C, m.p. 245°C (decomp) (0.12 g; 43%). Found: C, 65.9; H, 5.5 (calcd. for $C_{39}H_{39}BOs$: C, 66.1; H, 5.6%. Λ_m (10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 48 S cm^2 mol^{-1}.

η-Benzene-η-cyclopentadienylosmium(II) tetraphenylborate (m.p. 125—126°C (0.12 g; 17%). Found: C, 63.1; H, 4.5. Calcd. for $C_{35}H_{31}BOs$: C, 64.4; H, 4.8%) was similarly prepared from $[\{Os(\eta\text{-}C_6H_6)Cl_2\}_2]$, $Tl[C_5H_5]$ and $Na[BPh_4]$.

η^5-Cyclohexadienyl-η-cyclopentadienylruthenium(II)

The complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ [5] (0.20 g; 0.72 mmol) was dissolved

in 1,2-dimethoxyethane (50 cm^3) and $Na[BH_4]$ (0.24 g; 6.30 mmol) added in small amounts over a 20 minute period while the reaction mixture was stirred under nitrogen. After 4 hours, water was added to destroy the excess of $Na[BH_4]$ and the solvent removed under vacuo to give a dark brown residue. On shaking this with petroleum ether (b.p. 60—80°C) a very small amount of the product was extracted and removal of solvent gave a yellow solid (ca. 5% yield). ^1H NMR in $CDCl_3$ at 301 K: 5.79 (m) (H_4), 4.72s (η-C_5H_5); 4.43(m), (H(3,5)); 2.25(m) (H(2,6), H(1) *exo* and *endo*)



Mass spectrum *m/e* (based on ^{102}Ru peak): 245 ($[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$); 167 ($[Ru(\eta\text{-}C_5H_5)]^+$); 123 ($[Ru(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]^{2+}$). Trace amounts of this product were also obtained when $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$ was treated with $Na[BH_4]$ in various solvents (tetrahydrofuran, dioxane). No evidence however for even trace amounts of $[Os(C_6H_7)(C_5H_5)]$ was found on treatment of $[Os(\eta\text{-}C_6H_6)(C_5H_5)]BPh_4$ with $NaBH_4$ in various solvents.

Similarly, reaction of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations with other nucleophiles (Y) such as CN^-, OH^- and various PR_3 gave either no evidence for reaction (M = Ru; Y = PR_3; M = Os, Y = PR_3, CN^-, OH^-) or extensive decomposition involving displacement of both carbocyclic rings (M = Ru; Y = CN^-, OH^-).

Electrochemical investigation

Electrochemical studies were carried out using a Princeton Applied Research (PAR 170) instrument. All solutions were degassed with argon prior to measurement to remove dissolved oxygen. The electrolyte solution was tetrabutylammonium tetrafluoroborate ($TBABF_4$) in either CH_2Cl_2, CH_3CN or CH_3NO_2 and the reference electrode was Ag/AgI (using this reference electrode, ferrocene is oxidised at +0.60 V).

$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ in 0.25 M $TBABF_4/CH_3NO_2$. No cathodic response to —1.50 V; irreversible oxidation at $E_{1/2}$ + 0.58 V (100 mV s^{-1} scan rate) even at —24°C: remains irreversible at 100 V s^{-1} scan rate in 0.10 *M* $TBABF_4/CH_3CN$ but moves to +0.80 V in this solvent.

$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$; in 0.10 M $TBABF_4/CH_3CN$. No cathodic response to —2.60 V at —40°C. Irreversible oxidation at $E_{1/2}$ = +0.94 V (even at —40°C and 100 V s^{-1} scan rate).

$[Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ in 0.10 M $TBABF_4/CH_3CN$. No cathodic response on scanning to —2.60 V at —40°C. Irreversible oxidation at $E_{1/2}$ = +0.56 V (100 mV s^{-1} scan rate). Remains irreversible at —40°C.

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We thank Johnson-Matthey Ltd. for loans of ruthenium trichloride and sodium hexachloroosmate(IV), the SRC (D.A.T.) and the University of Edinburgh (I.W.R) for research studentships, Dr. D. Vattkis for help with the electrochemical measurements and Dr. D.R. Robertson for some preliminary results.

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Preliminary communication

PREPARATION, X-RAY STRUCTURAL ANALYSIS AND SOME PROPERTIES OF DICHLOROTETRAKIS(n-BUTYRATO)DIOSMIUM(III)

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The paramagnetic compounds $[Os_2(OCOR)_4Cl_2]$ (R = n-C_3H_7, C_2H_5, CH_2Cl) have been synthesised by reaction of $[Os(OCOCH_3)_2Cl]_n$ with the appropriate acids and the binuclear tetracarboxylate bridged structure confirmed by X-ray analysis for R = n-C_3H_7, (Os—Os distance 2.301 Å; cf. the related $[Os_2(hp)_4Cl_2]$-$(CH_3CN)_2$; Os—Os, 2.357 Å) (hp = 2-hydroxypyridine anion).

In the last two decades, extensive studies on binuclear complexes containing multiple metal-to-metal bonds have been published [1]. However, until the recent report of the crystal structure of $[Os_2(hp)_4Cl_2]$, (hp = 2-hydroxypyridine anion) [2], no examples of such complexes containing osmium had been found.

In this preliminary communication, we now wish to report the preparation, X-ray structural analysis and some properties of the closely related $[Os_2(OCO\text{-}n\text{-}C_3H_7)_4Cl_2]$ (I) compound. This was prepared in reasonable yield (50—60%) by reaction at 140°C for 8 h of the sparingly soluble $[Os(OCOCH_3)_2Cl]_n$* with an excess of n-butyric acid. On cooling the solution slowly, dark green needle-shaped crystals of the product are deposited. Similar reactions with propionic and monochloroacetic acid give the corresponding $[Os(OCOR)_2Cl]_n$ (R = C_2H_5 (25%), CH_2Cl (50%)). As for the acetate complex [3,4] the latter compounds are not sufficiently soluble for molecular weight determination** but for compound I, osmometric molecular weight measure-

*This complex, prepared in 25% yield in our laboratory [3], by reaction of $Na_2[OsCl_6]$ with acetic acid/acetic anhydride has been obtained very recently [4] in higher yield (55%) by addition of a little concentrated hydrochloric acid to this reaction mixture.

**However, in the mass spectra of all these compounds the appearance of the parent ions $[Os_2(OCOR)_4Cl_2]^+$, together with fragmentation patterns corresponding to successive loss of two chloride groups strongly support their formulation as binuclear species.

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ments in benzene confirmed the retention in solution of the binuclear unit established by X-ray structural analysis.

Crystal data for I: $C_{16}H_{20}Cl_2O_8Os_2$, monoclinic, space group $P2_1/n$ with cell parameters, a = 6.789(2), b = 11.790(1), c = 14.923(1) Å, β = 98.211(18)°, U = 1182 Å^3, Z = 2, D_c = 2.25 g cm^{-3}; monochromated Mo-K_α radiation 0.71069 Å, μ = 116.8 cm^{-1}.

Structure determination: A crystal of dimension 0.35 × 0.18 × 0.04 mm was used to collect 2100 unique data out to θ = 25° on a CAD 4 diffractometer. An empirical absorption correction was applied. The structure was solved by Patterson and difference Fourier methods. All non-hydrogen atoms have been located and refined anisotropically to give R = 0.044 from the 1686 reflections with $I > 2.5\sigma(I)$. The weighting scheme was $w = 1.0/(\sigma^2(F) + 0.00089\ F^2)$ Fractional coordinates are given in Table 1 and selected bond lengths and angles in Table 2.

The molecule is a dimer lying on a crystallographic inversion centre with each osmium ion exhibiting octahedral coordination (Fig. 1). The Os—Os and Os—Cl distances of 2.301 and 2.417 Å, respectively, are comparable with those found in the related $[Os_2(hp)_4Cl_2]2CH_3CN$ (2.357 and 2.505 Å, respectively) [2]. The butyrate shows both trans (C(8)—C(7)—C(6)—C(5) = 176°) and gauche (C(4)—C(3)—C(2)—C(1) = 54°) conformations.

Interestingly, variable temperature magnetic measurements from 300—188 K

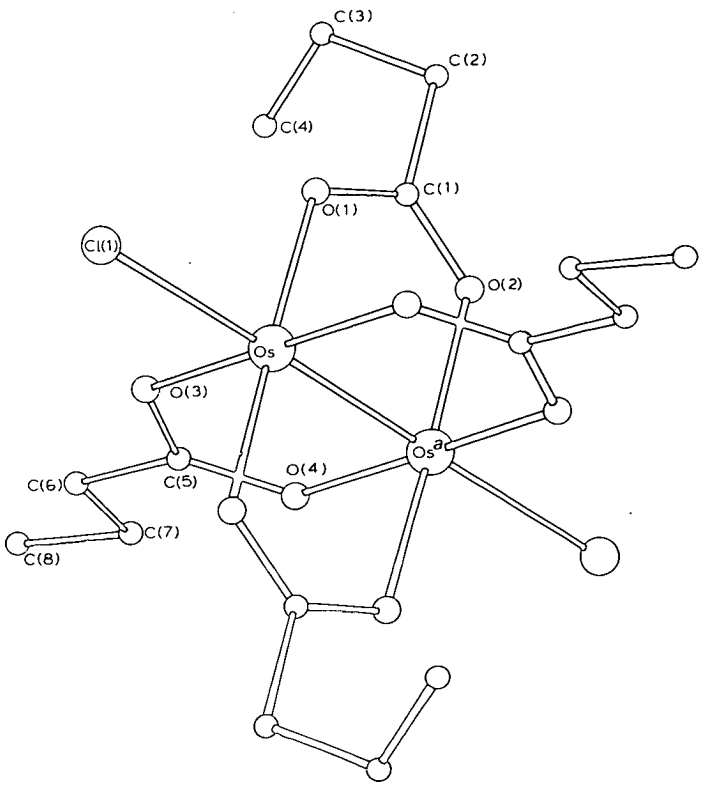

Fig. 1. Molecular structure of $[Os_2(OCO\text{-}n\text{-}C_3H_7)_4Cl_2]$.

TABLE 1

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS

	x	y	z
Os	0.08828(6)	0.44036(4)	0.45944(3)
Cl(1)	0.2845 (6)	0.3171 (3)	0.3776 (3)
O(1)	−0.1208 (12)	0.4622 (7)	0.3504 (6)
O(2)	−0.2921 (12)	0.5767 (6)	0.4292 (6)
C(1)	−0.2664 (18)	0.5238 (10)	0.3565 (8)
C(2)	−0.4205 (20)	0.5423 (13)	0.2736 (10)
C(3)	−0.3295 (28)	0.5942 (19)	0.1989 (12)
C(4)	−0.2152 (30)	0.6979 (16)	0.2219 (15)
O(3)	0.2344 (13)	0.5736 (6)	0.4192 (6)
O(4)	−0.0672 (12)	0.3092 (6)	0.5015 (6)
C(5)	0.1977 (18)	0.6709 (11)	0.4461 (9)
C(6)	0.3123 (20)	0.7659 (11)	0.4113 (12)
C(7)	0.2366 (23)	0.8809 (14)	0.4287 (13)
C(8)	0.3576 (27)	0.9675 (14)	0.3840 (13)

TABLE 2

BOND LENGTHS (Å) AND BOND ANGLES (°)

Bond lengths (Å)	
Os—Os	2.301(1)
Os—Cl(1)	2.417(3)
Os—O(1)	2.018(8)
Os[a]—O(2)	2.015(8)
C(1)—O(1)	1.241(14)
C(1)—O(2)	1.284(15)
C(1)—C(2)	1.518(25)
C(2)—C(3)	1.482(21)
C(3)—C(4)	1.462(26)
Os—O(3)	1.996(7)
Os[a]—O(4)	2.022(8)
C(5)—O(3)	1.252(14)
C(5)—O(4)	1.284(15)
C(5)—C(6)	1;499(18)
C(6)—C(7)	1.486(21)
C(7)—C(8)	1.523(25)
Bond angles (°)	
Cl(1)—Os—Os[a]	177.96(10)
O(1)—Os—Os[a]	89.27(23)
O(2)—Os—Os[a]	88.55(23)
O(3)—Os—Os[a]	89.79(24)
O(4)—Os—Os[a]	88.23(23)
Os—O(1)—C(1)	119.41(8)
O(1)—C(1)—O(2)	123.5(10)
C(1)—O(2)—Os[a]	119.2(7)
Os—O(3)—C(5)	119.6(8)
O(3)—C(5)—O(4)	123.3(11)
C(5)—O(4)—Os[a]	119.04(8)

[a] Represents the atom related by $\bar{x}$, $\bar{y}$, $\bar{z}$.

on dichloromethane solutions of the butyrate and propionate (by Evans' method [5]) reveal that both compounds are paramagnetic. However, the magnitude of μ_{eff} (e.g. for R = n-C_3H_7, μ_{eff} decreases from 1.15 BM/Os at 300 K to 1.02 BM/Os at 188 K), is indicative of considerable antiferromagnet-

ic interactions between the osmium(III) ions*. Although further studies, both in the solid state and over a wider range of temperatures, are now required to substantiate these data, it seems reasonable to suggest for these $[Os_2(OCOR)_4Cl_2]$ complexes that there is an appreciable population of a spin triplet state, (perhaps corresponding to the central electronic configuration $\sigma^2\pi^4\delta^2\pi^{\star 2}$** or $\sigma^2\pi^4\delta^2\delta^{\star 1}\pi^{\star 1}$), at higher temperatures with the singlet ground state, (arising from the $\sigma^2\pi^4\delta^2\delta^{\star 2}$ configuration), becoming increasingly favoured as the temperature is lowered.

Furthermore, cyclic voltammetric and alternating current voltammetric studies on I in CH_2Cl_2/0.25 *M* n-Bu_4NBF_4 at 20°C show a one-electron, reversible oxidation (+0.53 V)*** but no further redox steps are observed up to the solvent limit, even at 208 K. For $[Os_2(OCOC_2H_5)_4Cl_2]$, however, in addition to the reversible oxidation step at +0.57 V, irreversible oxidation and reduction waves are found at +1.28 and −1.54 V, respectively.

Although there is no electrochemical evidence for formation of stable formally mixed-valence $[Os_2(OCOR)_4Cl_2]^-$ anions, (cf. the X-ray analysis of $Cs[Ru_2(OCOMe)_4Cl_2]$ [8]), the recent brief report [4] of the synthesis of $[Os_2(OCOMe)_4Cl(C_5H_5N)]$ and $[Os_2(OCOMe)_4(C_5H_5N)_2]Cl$ from $[Os_2(OCOMe)_2Cl]_n$ illustrates that a range of such $Os_2^{II,III}$ (or $Os_2^{2.5+}$) complexes can be readily isolated. Therefore, comparative studies of their magnetic and optical properties with those of the unusual $[Os_2^{III,IV}(OCOR)_4Cl_2]^+$ cations are now planned.

Finally, preliminary studies show that, like the related binuclear transition metal carboxylates $[M_2(OCOR)_4]$ (M = Mo, Rh etc.) [1], the carboxylate bridges in $[Os_2(OCOR)_4Cl_2]$ are readily replaced by a variety of potential bidentate ligands. For example, reaction of I with $Na[S_2CNMe_2]$ gives $[Os(S_2CNMe_2)_2Cl]_n$ and further studies on the physicochemical properties of such compounds are now in progress.

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*Under the same conditions *mer*-$[OsCl_3(PMe_2Ph)_3]$ shows the behaviour expected for a magnetically dilute osmium(III) complex [6] i.e. μ_{eff} = 1.70 BM (almost temperature invariant).

**In support of this proposal, recent SCF-Xα-SW calculations on $[Ru_2(O_2CH)_4]^+$ etc. and related species indicate an electronic configuration $\sigma^2\pi^4\delta^2\pi^{\star 2}\delta^{\star 1}$ with a very small energy separation between the $\pi^\star$ and $\delta^\star$ orbitals [7].

***All $E_{1/2}$ values are measured with respect to a Ag/AgI reference electrode at which ferrocene is oxidised at +0.60 V.